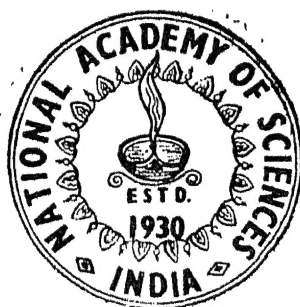


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SECTION - A

PART I



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SECTION - A

PART I

STUDY OF THE COMPONENT ACIDS FROM THE BODY FAT OF THE
FISH LABEO ROHITA WITH DIFFERENT STAGES OF GROWTH

By

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[Received on 25th August, 1962]

ABSTRACT

A good deal of variations in the fatty acid composition of the fish fats have been reported with the change in place and climatic conditions and also even in the same fish different parts have different fatty acid composition. It has also been observed that the variation is common with different states of maturation of the fish. Keeping all this in view an attempt has been made to study the variations in the component fatty acids from the body fat of the fish *Labeo rohita* under different stages of growth.

Changes in the chemical composition of the fish fat with different habitat and climate have been reported.¹ Lovern² has reported the variation in the chemical composition of the fat obtained from the same fish during different parts of the year with reference to Herring oil. Black and others³ have studied the variations in the fatty acid composition with the growth of the fish pilchard (*Sardina ocellata*). Fats obtained from different parts of the same fish have different fatty acid composition.⁴ Fatty acid composition of fish fat varies in mature as well as in embryonic stages as has been shown in the study of the liver fats from the mature and the embryonic sharks.⁵

In the present paper a detailed study of the component acids of the body fat obtained from the different stages of growth of the fish *Labeo rohita* has been reported. The following points have been kept in view in connection with the collection of the material.

- (1) The fish were collected from the same environment,

- (2) They were collected during the same period of the year, which for the purpose of the present work was the last fortnight of June every year.
- (3) A constant change in weight was the main guiding factor in the collection of the material for different stages.

Although the studies on the age and growth of the fish have been reported in a large number of cases from foreign countries,⁶ in India such a type of study has been done only in the case of *Mrigala* (Ham.) and a few other species.⁷

As the fish *Labeo rohita* has not been studied from this point of view, the age of the fish could not be approximated with regard to the furcal length, breadth and weight. Under these circumstances, the variation of weight by a constant factor (in this case about 500 gms.) was the only possible criterion of classification into different stages.

The average length, breadth and weight for different stages are shown below :

TABLE 1

Measurements	Stage No.					
	1	2	3	4	5	6
Length (cms.)	28.2	35.9	41.3	51.2	53.4	56.6
Breadth (cms.)	19.5	23.1	26.3	30.0	33.0	35.4
Weight (gms.)	500.1	1044.0	1564.0	2024.0	2483.0	2908.0

EXPERIMENTAL

Fish was cut lengthwise on its ventral side. Viscera was removed from the fish and the liver was removed from the visceral portion. The liver-removed visceral portion and the liver were kept separately in acetone. The body of the fish was cut into small pieces and minced and the minced tissue was extracted with acetone on a steam bath two to three times. The acetone extract was separated and the solvent was distilled off. The residual mass was taken up in petroleum ether (b.40–60°) which dissolved the fat. The acetone refluxed tissue was also refluxed with petroleum ether to dissolve the fat and this extract was mixed with the previous petroleum ether extract. The combined petroleum ether extracts were dried by means of anhydrous sodium sulphate, the solvent was distilled off and the recovered fat was kept in vacuum.

The analytical characteristics of the fats were determined by the usual standard methods.

Fat was saponified and the fatty acids were recovered from the soap solution on decomposition with 10% sulphuric acid solution and subsequent extraction with ether. The fatty acids were resolved into three main groups, A

B and C by the joint application of lithium salt-acetone method⁶ followed by the Hilditch's modification of the Twitchell's⁹ lead salt-ethanol process.

Acids of each main group were converted into their methyl esters and subsequently fractionated under reduced pressure. Iodine value and saponification value determinations were made on each fraction of the three main groups. The mean unsaturation expressed by the fractional number of hydrogen atoms short of saturation was determined as usual by interpolation and extrapolation from the respective ester fractions in each group from which the mean of the equivalent of the homologous ester groups (C₁₄, C₁₆, C₁₈, C₂₀, C₂₂, and C₂₄) follows.

Analytical characteristics of the body fats, from the different stages of the fish *Labeo rohita* are given in table II.

TABLE II

Analytical consants	Stage No.					
	1	2	3	4	5	6
% fat	2.80	2.93	2.96	3.24	3.86	3.89
Acid value	2.71	3.81	4.40	4.39	3.75	3.60
Iodine value	102.4	106.1	107.7	105.6	106.7	104.8
Sap. value	196.7	191.9	182.3	189.0	189.4	184.8
Hehner value	89.90	89.84	89.89	90.40	90.46	89.99

TABLE III

Analytical characteristics of the mixed acids of the body fats from the six stages of the fish *Labeo rohita*.

Analytical constants	Stage No.					
	1	2	3	4	5	6
Saponification value	201.8	194.5	189.7	193.0	194.7	196.7
Iodine value	109.7	110.9	115.6	110.9	111.1	112.8

A detailed account of the data of fractionation of methyl esters (and their calculated composition) of the three main groups of acids from the mixed acids of the body fat of the fish *Labeo rohita* of stage No. 1 are given in tables V, VI, VII and VIII. Similarly the data for the body fats of the remaining five stages were tabulated but to economise space only % W/W of the component acids (excluding NSM) of the body fats of the six stages are given in table IX for comparison.

TABLE IV

Resolution of mixed acids into three main groups with their analytical constants.

Stage No.	A			B			C		
	Wt. %	N. V.	I. V.	Wt. %	N. V.	I. V.	Wt. %	N. V.	I. V.
1	28.4	283.8	190.4	42.0	281.9	125.8	29.6	271.3	21.4
2	24.4	290.3	215.1	44.5	285.6	118.4	31.1	275.8	22.4
3	20.3	297.4	201.6	52.3	288.7	137.4	27.4	264.9	18.7
4	23.6	287.0	195.4	43.1	281.7	124.5	33.3	278.1	20.6
5	26.0	285.1	249.7	39.3	273.1	126.8	34.7	264.7	23.7
6	24.0	290.6	230.4	41.6	275.4	149.8	34.4	267.8	21.7

TABLE V

Fractionation of methyl esters of Lithium salt-acetone soluble group (A) and calculated composition of ester fractions.

Fr. No.	Wt.	S. E.	I. V.	Unsaturated				
				C ₁₆	C ₁₈	C ₂₀	C ₂₂	NSM
1	2.16	279.4	146.1	1.13	1.03
2	1.62	284.6	152.3	0.54	1.08
3	1.93	288.1	159.8	0.40	1.53
4	2.10	294.6	168.1	...	2.05	0.05
5	2.08	299.9	180.4	...	1.57	0.51
6	1.95	306.1	200.9	...	0.99	0.96
7	1.49	315.9	219.4	...	0.21	1.28
8	1.96	336.1*	248.9	1.17	0.75	0.04
15.29				Wt.	2.07	8.46	3.97	0.75
				%esters	13.54	55.34	25.96	4.90
				%acids	13.46	55.30	26.04	4.93
				%in mixed acids	3.83	15.71	7.40	1.40
								0.08
Unsaturated esters taken as :				S. E.	I. V.			
				C ₁₆	267.3	128.3		
				C ₁₈	294.0	172.8		
				C ₂₀	319.8	246.2		
				C ₂₂	346.5	274.9		

TABLE VI
Fractionation of methyl esters of Lead salt ethanol soluble group (B) and
calculated composition of ester fractions.

Fr. No.	Wt.	S. E.	I. V.	Saturated			Unsaturated				NSM	
				C ₁₆	C ₁₈	C ₂₀	C ₁₆	C ₁₈	C ₂₀	C ₂₂		
1	3.16	274.8	83.4	0.23	0.05	...	2.12	0.76	
2	2.75	280.6	94.6	0.07	0.05	...	1.37	1.26	
3	3.33	288.7	95.8	0.06	0.12	...	0.72	2.43	
4	4.18	296.1	99.4	0.01	0.19	3.89	0.09	...	—	
5	3.56	301.4	110.6	...	0.19	0.02	...	2.56	0.79	...	—	
6	2.97	304.6	128.7	1.89	1.08	...	—	
7	1.79	314.6	139.6	0.46	1.33	—	—	
8	1.88	329.4*	164.6	1.57	0.29	0.02	
23.62				Weights	0.37	0.60	0.02	4.21	13.25	4.86	0.29	0.02
				%esters	1.57	2.54	0.08	17.82	56.11	20.57	1.23	0.08
				%acids	1.56	2.54	0.09	17.74	56.10	20.65	1.24	0.08
				%in mixed acids	0.66	1.07	0.04	7.45	23.56	8.67	0.52	0.03
Unsaturated esters taken as :												
				S. E.	I. V.							
				C ₁₆	268.0		94.8					
				C ₁₈	295.6		103.1					
				C ₂₀	321.8		165.8					
				C ₂₂	348.0		219.0					

TABLE VII
Fractionation of methyl esters of Lead salt-ethanol insoluble group (C) and
calculated composition of ester fractions :

Fr. No.	Wt.	S. E.	I. V.	Saturated				Unsaturated				NSM	
				C ₁₄	C ₁₆	C ₁₈	C ₂₀	C ₁₄	C ₁₆	C ₁₈	C ₂₀		
1	2.57	264.7	8.75	0.40	1.93	—	—	0.03	0.21	—	—	—	
2	2.37	267.3	10.34	0.18	1.93	—	—	0.01	0.25	—	—	—	
3	4.30	274.1	13.74	—	3.08	0.58	—	—	0.49	0.15	—	—	
4	3.41	281.5	14.95	—	1.61	1.24	—	—	0.28	0.28	—	—	
5	3.28	287.4	18.47	—	0.92	1.67	—	—	0.20	0.49	—	—	
6	2.18	295.5	22.90	—	0.13	1.47	—	—	0.01	0.57	—	—	
7	2.17	306.1	30.70	—	—	0.95	0.41	—	—	0.50	0.31	—	
8	1.31	313.4*	37.80	—	—	0.42	0.28	—	—	0.32	0.27	0.02	
21.59				Wts.	0.58	9.60	6.33	0.69	0.04	1.44	2.31	0.58	0.02
				%esters	2.73	44.46	29.31	3.19	0.18	6.66	10.70	2.68	0.09
				%acids	2.71	44.35	29.39	3.21	0.18	6.64	10.73	2.70	0.09
				%in mixed acids	0.80	13.12	8.69	0.95	0.05	1.96	3.18	0.80	0.03

All unsaturated esters taken as monoethenoids

*Equivalents of esters freed from NSM A₈=329.7 ; B₈=325.6 ; C₈=308.4

TABLE VIII

Acids	Component acids			Sum %	Whole fat excluding unsaponifiable matter	
	A	B	C		W/W (%)	Moles (%)
Myristic	—	—	0.80	0.80	0.80	0.98
Palmitic	—	0.66	13.12	13.78	13.80	14.99
Stearic	—	1.07	8.69	9.76	9.77	9.57
Arachidic	—	0.04	0.95	0.99	0.99	0.88
Unsaturated fractions						
C ₁₄	—	—	0.05	0.05	0.05	0.06
C ₁₆	3.83	7.45	1.96	13.24	13.26	14.53
C ₁₈	15.71	23.56	3.18	42.45	42.51	42.07
C ₂₀	7.40	8.67	0.80	16.87	16.90	15.31
C ₂₂	1.40	0.52	—	1.92	1.92	1.61
NSM	0.08	0.03	0.03	0.14	—	—
Mean unsaturation of :						
C ₁₄	—	—	-2.0	-2.0		
C ₁₆	-2.7	-2.0	-2.0	-2.2		
C ₁₈	-4.0	-2.4	-2.0	-3.0		
C ₂₀	-6.2	-4.2	-2.0	-5.0		
C ₂₂	-7.5	-6.0	—	-7.1		

TABLE IX
Component acids excluding non saponifiable matter (%W/W)

Acids	Stage No.					
	1	2	3	4	5	6
Myristic	0.80	0.12	1.84	0.62	2.76	1.88
Palmitic	13.80	14.85	14.62	14.33	17.49	20.18
Stearic	9.77	11.50	9.12	13.40	6.93	9.03
Arachidic	0.99	1.33	0.48	3.04	1.89	0.24
Unsaturated fractions						
C ₁₄	0.05	—	0.11	0.01	0.65	0.60
C ₁₆	13.26	8.67	9.74	12.41	26.23	24.43
C ₁₈	42.51	39.65	40.02	37.73	30.48	23.83
C ₂₀	16.90	23.32	19.12	17.34	9.07	15.44
C ₂₂	1.92	0.56	4.95	1.12	3.93	4.37
C ₂₄	—	—	—	—	0.57	—

DISCUSSION

The fatty acid composition of the body fats of the fish *Labeo rohita* shows resemblance with other fats of aquatic origin,¹⁰ in that the fats contain C_{16} , C_{18} and C_{20} as the major and C_{14} and C_{22} as the minor unsaturated acids. The proportion of C_{22} unsaturated acids usually increases at the later stages in case of body fats and some C_{24} unsaturated acids are also found to occur towards the fifth stage (Table IX).

The major component saturated acid in the fats of aquatic origin is palmitic (10 to 18%) while myristic and stearic acids are present in minor proportions¹¹ (1 to 2%). In the body fats of this fish the percentage of palmitic acid is a bit higher (14 to 20%). A significant difference is in the high percentage (7 to 13%) of stearic acid. Arachidic acid though a minor component is inevitable and has been reported in a number of Indian fresh water fishes.¹² The distinctive features of the fresh water fish fats are the small proportions of unsaturated C_{20} acids, the predominance of unsaturated C_{18} and C_{16} acids. Although the small proportions of C_{22} unsaturated and predominance of unsaturated C_{18} acids (24-40%) are maintained in the present case, the unsaturated C_{20} acids are not present in reduced proportions (10 to 23%).

A comparison of the component fatty acids of the fats from the sea water life and the fresh water life reveals significant differences in that the fats of aquatic animals, large or small, differ typically in the proportions of certain component acids according to whether the habitat of the animals is salt or fresh water. In the marine fats C_{16} and C_{18} unsaturated acids are less than those from fresh water fats while the C_{20} and C_{22} unsaturated acids are more in the marine than in the fresh water fish fats. The acids from the body fat of *Labeo rohita* show a similarity with the fats of marine mammalia such as Whale oil,¹³ in increased content of C_{18} unsaturated acids. The C_{18} unsaturated acids are present in considerable amount and the percentage of C_{20} unsaturated acids is almost comparable to that of C_{16} unsaturated acids (10-25%). The C_{22} unsaturated acids are however, in traces; in all cases less than 4.5%.

As a result of the analysis and examination of the body fats of the fish *Labeo rohita* of the six stages mentioned earlier, it has been observed that the iodine value of the fats remains practically between 102 and 107 indicating that although the proportions of different unsaturated acids undergo a change with the growth of the fish, the mean unsaturation of the fats remains the same. Saponification value shows a decrease in the second and third stages, then increases by about six units in the subsequent stages, which shows that after the third stage there is a tendency towards the formation of lower acids (Table II). This point is also borne out by the component acids of the body fat as shown in Table IX. In the second and third stages there is an increase in the proportions of C_{20} and C_{22} unsaturated acids but a small decrease in the amounts of C_{16} and C_{18} unsaturated acids and also there is a slight increase in the proportions of palmitic and stearic acids. It is also clear from the results (Table IX) that the change of unsaturated acids with different stages does not show any regular gradation. C_{18} unsaturated acids decrease progressively from the first to the sixth stage with the consequent increase of C_{20} or C_{22} unsaturated acids or both so that the mean unsaturation practically remains the same during different stages. The C_{16} unsaturated acids similarly show a decrease in the second stage and then gradually increase to 26%. The percentage of palmitic acid is almost constant

upto the fourth stage ; and then increases in the later stages. The arachidic acid which, as has been already explained, rarely occurs in foreign fish fats, but is a minor constituent of Indian fish fats, shows an irregular variation.

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STABILITY OF LYOPHOBIC COLLOIDS
PART I. STABILITY OF HYDROUS FERRIC OXIDE SOL IN THE
PRESENCE OF NON-ELECTROLYTES, ACETONE AND ETHYL ALCOHOL

By

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ABSTRACT

Samples of the sols of hydrous ferric oxide were prepared by three different methods, *viz.* by (i) Kreck's method, and by peptising with (ii) hydrochloric and (iii) acetic acid. The iron content of the sols and the pH were kept the same. Coagulation kinetics were studied with the help of Lumetron photoelectric-colorimeter, using potassium chloride as coagulating electrolyte, both in the presence and absence of ethyl alcohol and acetone. Sedimentation velocity of the coagulum was also noted with Leitz-E-Sedimentometer. It has been concluded that sensitisation and stabilisation produced by the added non-electrolyte is highly specific and is greatly influenced by the surface properties of the dispersed units which are different for the sol particles of the same substance, but obtained by different methods.

The influence of non-electrolytes on the stability of a sol is a vexed problem and holds out promise for further work. The stability of hydrous ferric oxide sols has largely been investigated by several workers. The precipitation value of an electrolyte has been considered to be important in describing the stability of a sol, which is considerably affected by the presence of some non-electrolytes. It has been noted that for a sol, this varies with the nature of the electrolyte and even with the time of observation, as has recently been investigated by Ghosh and coworkers (1, 2). The present investigation deals with the stability of colloidal hydrous ferric oxide as affected by the non-electrolytes, ethyl alcohol and acetone, towards potassium chloride in order to assess the nature of the sol particles as obtained by different methods *viz.* by Kreck's method and also by peptising the hydrous oxide either by hydrochloric or acetic acid.

EXPERIMENTAL

Three samples of hydrous ferric oxide sol were prepared (A) by Kreck's method and by peptising with (B) hydrochloric and (C) acetic acids. The iron contents of the sols were adjusted to 0.6518 gm of iron/litre by dilution and pH was also adjusted to 3.65 by dialysing the sols to different extents. The purity of the sols A and B were determined by estimating the ratio of iron to chloride present in these sols and were found to be 1.5322 and 0.7661 respectively. The stability of three sols towards its complete coagulation by potassium chloride solution was first determined and were as noted below :—

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TABLE 1

Temperature = 35°

Time of complete coagulation = 1 hour.

Volumes of sol taken = 5 ml.

Total volume = 30 ml.

Sample	Amount of potassium chloride required for complete precipitation.
A	2.6 ml 0.5 N KCl.
B	3.8 ml 0.1 N KCl.
C	6.0 ml N KCl.

A Lumetron photoelectric colorimeter model 402-E was employed to study the coagulation kinetics, operated on 115v with incandescent bulb of 100 C. P. the source of light. The emitted light was passed through a monochromatic filter (640 $m\mu$). The apparatus was calibrated with distilled water in the cuvette for 100 percent transmission. From the observed values of percentage transmission the optical density was calculated by the relation: Optical Density = $2 \log_{10} P$, where P is the percentage transmission. The transmission was noted at different intervals of time for the mixture containing 5 ml of sol, x ml KCl + (25 - x) ml of distilled water, so that the final volume was 30 ml. The observations were taken within thirty minutes after the addition of the electrolyte. The results obtained with the sols A, B, C are reproduced in figures (1 to 6). Experiments were

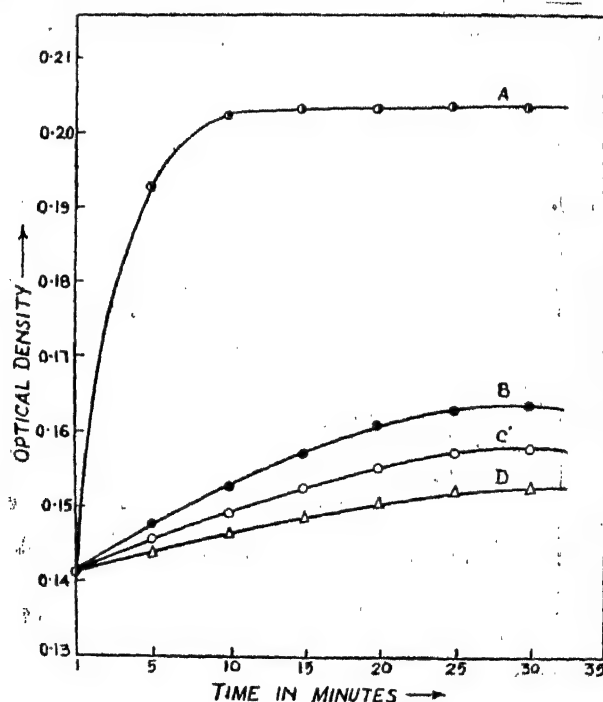


Fig. 1. Effect of Ethyl Alcohol on the Coagulation Kinetics of Sol A.
Curve A 0%; B 1.0%; C 3.0%; D 5.0% of ethyl alcohol,

[10]

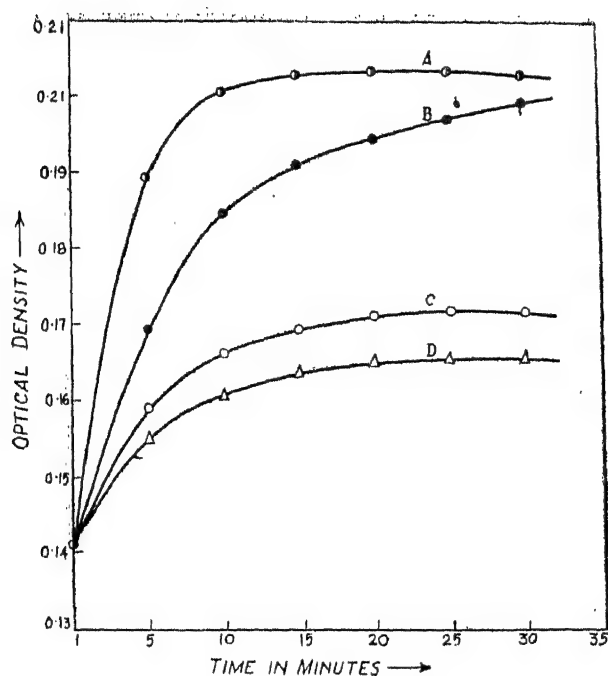


Fig. 2. Effect of Acetone on the Coagulation Kinetics of A.
Curve A 0% ; B 1.0% C 3.0% and D 5.0% of acetone.

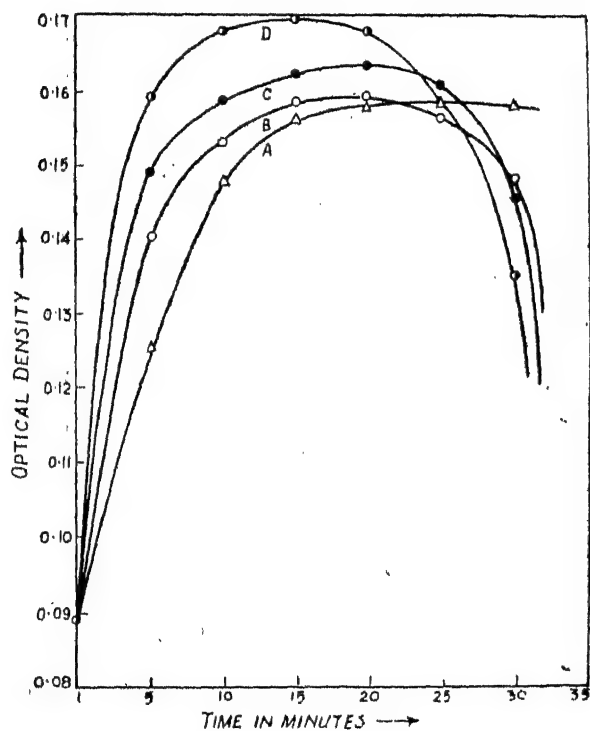


Fig. 3. Effect of Ethyl Alcohol on the Coagulation Kinetics of Sol B
Curve A 0% ; B 1.0% ; C 3.0% and D 5.0% of ethly alcohol.

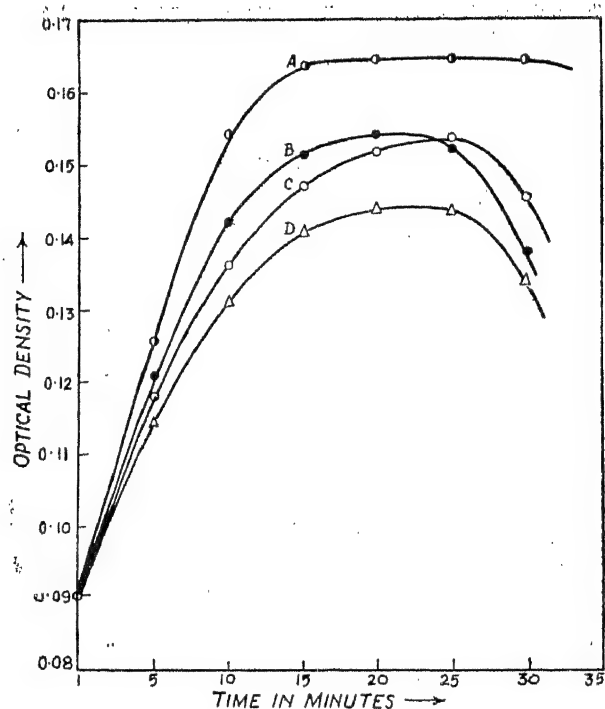


Fig. 4. Effect of Acetone on the Coagulation Kinetics of Sol B. Curve A 0% ; B 1.0% C 3.0% and D 5.0% of acetone.

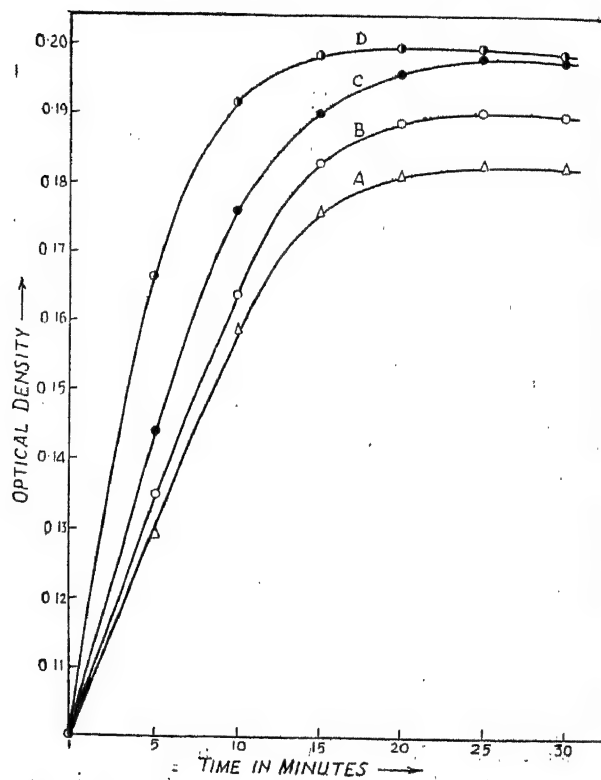


Fig. 5. Effect of Ethyl Alcohol on the Coagulation Kinetics of Sol C. Curve A 0% ; B 1.0% ; C 3.0% and 5.0% of ethyl alcohol.

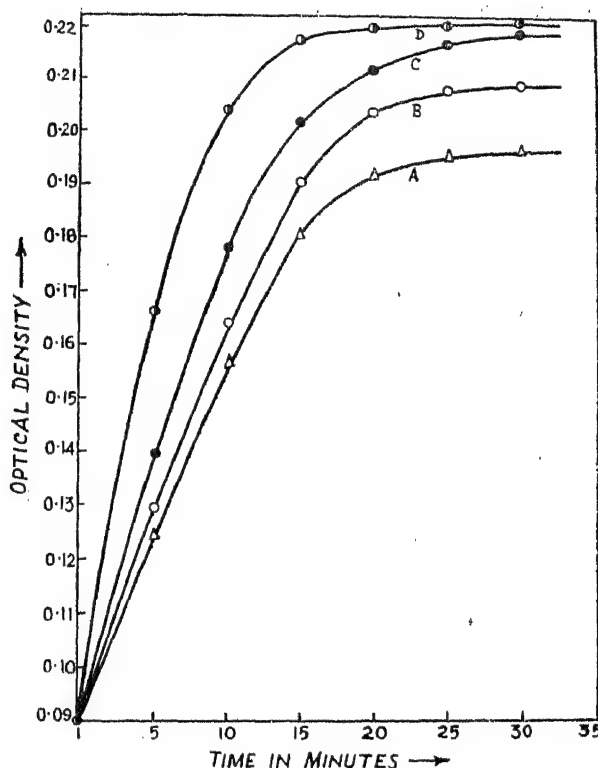


Fig. 6. Effect of Acetone on the Coagulation Kinetics of Sol C.
Curve A 0% ; B 1.0% ; C 3.0% and D 5.0% of acetone.

also performed with diluted sols by taking 2.5 ml of the sols in the final volume of 30 ml, and the results obtained show that the effect of the non-electrolytes becomes pronounced in the case of dilute sols.

It was noted in these experiments that as the coagulation process started there was an increase in the optical density. In the case of sol B, however, the optical density reached a maximum value and then decreased. There was no settling of the precipitate within thirty minutes of observation for the sols A and C but partial coagulation occurred in the case of the sol B.

In the course of these experiments it was also noted that the sols A, B and C yielded precipitates after coagulation which differed remarkably both in character and colour. Hence, the same amount of coagula obtained by coagulating the different sols by such amounts of potassium chloride which required one hour for complete coagulation, were collected and were shaken with a fixed volume of distilled water. The rate of sedimentation of the three suspensions were recorded with the help of Leitz E-Sedimentometer. The results have been reproduced

in fig. 7 and shows that the rate of settling of the coagula of the different sols are in the order : Sol A > Sol B > Sol C.

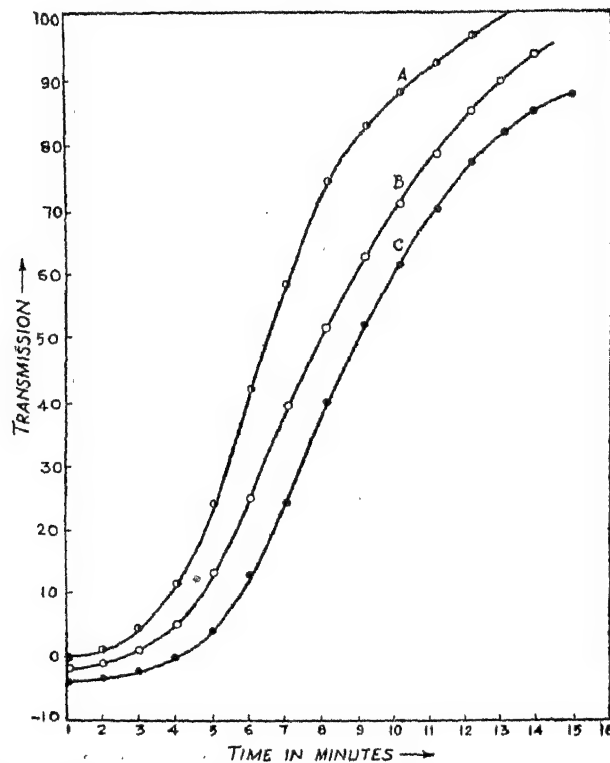


Fig. 7. Sedimentation Velocity of the Coagula of the sols A, B and C.

The microphotographs of these coagula were also taken and are given in plates 1-3.

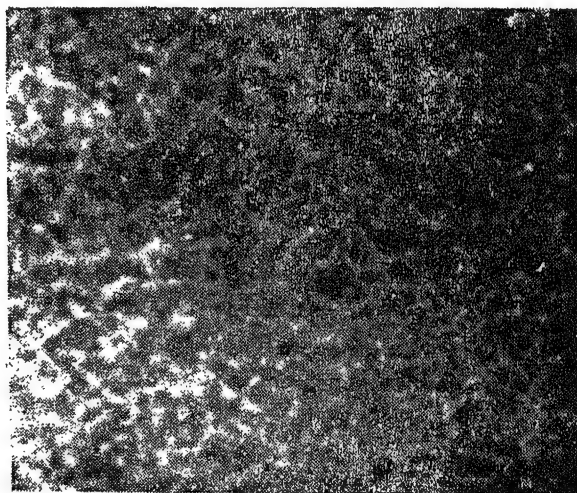


Plate No. 1 Sol A (Magnified 224 times).

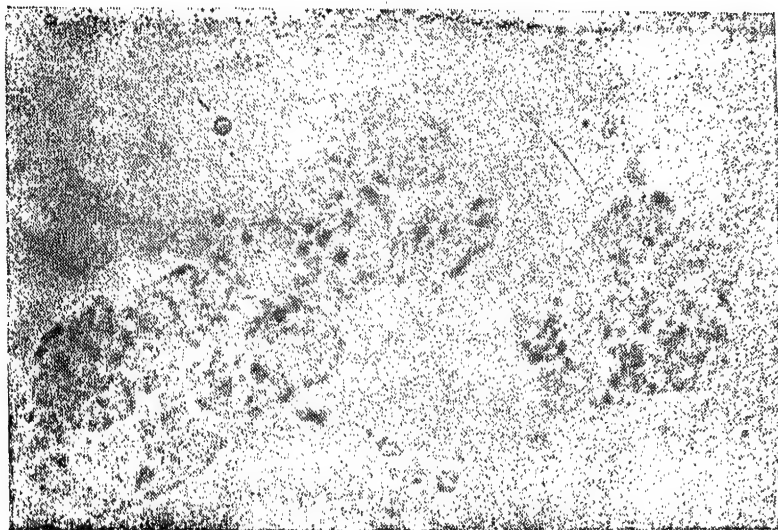


Plate No. 2 Sol B (Magnified 224 times).

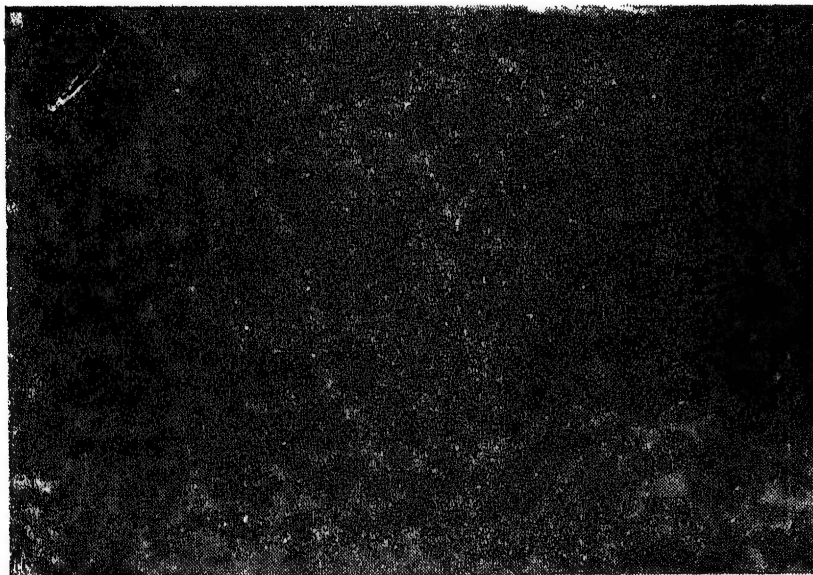


Plate No. 3 Sol C (Magnified 224 times).

It is clear that whilst in general the particles of the coagula obtained from the Sol A and B are large, those from the Sol C are smaller in size and a more compact and flocky structure is formed in the latter case.

SUMMARY OF THE RESULTS

The following conclusions are drawn from the above observations :

The sols of hydrous ferric oxide obtained by the various methods are different in their physical and chemical properties. As the pH and iron contents of the sol samples A, B and C were the same, the difference in their behavior towards the same non-electrolyte is due to the difference in the surface properties of the dispersed colloidal unit, ethyl alcohol sensitises sol A, whereas it stabilises sol B and C. Acetone, however, sensitises sols A and B but stabilisation is observed in the case of sol C. The extent of sensitisation or stabilisation produced increases with the increasing amount of non-electrolyte. The nature and shape of the coagula of the sols A, B, C, are different. The particles of sol A being comparatively heavier and larger than these of sol C, settles more rapidly. Further, the stability of these sols against coagulating electrolyte *viz.* potassium chloride also varies. Sol C being most stable while sol B is least stable among the three.

It is concluded that the hydrous ferric oxide sols prepared by different methods behave differently both in their physical and chemical properties. The method of the preparation of a particular sol has to be taken into consideration while defining its stability. The sensitisation or stabilisation produced by the added non-electrolyte is highly specific for the sols of hydrous ferric oxide, prepared by different methods and is dependent upon the surface properties of the dispersed colloidal units, which are different for the sol particles of the same substance obtained by different methods.

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PHYSICOCHEMICAL PROPERTIES OF MILK : PART I. COAGULATION OF COW'S MILK WITH VARIOUS ELECTROLYTES

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ABSTRACT

Milk was coagulated by hydrochloric acid and two zones of coagulation were observed at two widely varying concentrations of coagulant. While studying dilution effect on milk, normal dilution law was found applicable in the first zone, whereas in the second zone reverse was the case. Charge reversal took place in the second zone of coagulation, the milk underwent a change of charge from negative to positive value near about the second zone of coagulation. To determine the effect of mixing natural milk with liquified powered milk both whole and skimmed, the coagulation of these milks and their mixtures with pure milk was studied. The coagulants used were lead nitrate, lead acetate, zinc sulphate and aluminium chloride. The powdered milks both whole and skimmed also obeyed the normal dilution law in the first zone of coagulation. The skimmed milk was found to be a bit more stable than pure milk.

There are no suitable routine methods for distinguishing reconstituted milk from natural milk. An attempt was made by Choi and coworkers¹ to distinguish reconstituted milk by determining ferricyanide reducing (P. R. S.) value. It was found that a P. R. S. value of 4.07 mgm. of potassium-ferricyanide per 100 ml of milk was the maximum for normal pasteurized milk.

A value above this indicates either successive heating of milk during pasteurization or the presence of any form of processed milk solid. When the precise condition used for pasteurization is not known, detection of un-denatured whey proteins and the nitrogen content of milk will help to differentiate between the above two possibilities. The freezing of the samples give variable values.² Hence it is clear that a satisfactory method for distinguishing between reconstituted milk and pasteurized milk has yet to be developed.

With this end in view, it was thought necessary to study the physico-chemical properties of both reconstituted and pasteurized natural milk. Several attempts have been made to study the physical properties of milk. Measurements of density³, viscosity,⁴ surface tension,⁵ electrical conductivity,⁶ pH,⁷ freezing point,⁸ coagulation by rennet and electrolytes,⁹ determination of size distribution of fat globules¹⁰ and circular paper chromatography¹¹, have been used for the purpose of detection of adulteration in milk.

It will be reasonable to assume that in liquified milk both from skimmed and whole milk powders, the size of the globules and their stabilities may not be the same as in the case of pure milk and that the partial coagulation of the different types of milks mentioned above may not occur simultaneously. It may, therefore, be possible to separate these in a mixture by coagulation. Hence it was proposed to study the coagulation of pure cow's milk obtained from the same source and pure milk diluted with distilled water, liquified milk from whole milk and skimmed milk powders and also the mixtures of pure with whole and skimmed milk powders to find out if a differentiation could be made.

EXPERIMENTAL

Cow's milk from the same animal was collected and it was warmed up to 70°C at ordinary atmospheric pressure for five minutes so that curdling may be prevented for 10 hours. As a first step towards the detailed study of the physico-chemical properties of various kinds of milks, their coagulations with electrolytes were studied at room temperature. In order to study coagulation by electrolytes, we used two sets of test tubes thoroughly cleaned and washed by alkali and then chromic acid and finally several times with distilled water and then dried by keeping overnight in an inverted position. In one set of test tubes, were taken requisite quantities of the various electrolytes together with sufficient quantity of distilled water so as to make up 5 ml. In the other set of test tubes 5 ml of the particular milk of which coagulation was to be studied were taken. The contents of the test tube containing electrolyte after shaking well were poured gradually in the milk, the whole mixture then poured back again in the test tube containing electrolyte and finally the mixture was again poured back into the test tube containing the milk and allowed to stand for coagulation. That concentration of electrolyte was taken to be the coagulation concentration, in which the visible clotting was observed after one hour by viewing the test tube from the front when a 100 watt electric lamp was kept at a distance of one foot at the back (at the time of observation).

RESULTS AND DISCUSSIONS

Detailed results with pure milk are given in Table I with HCl.

From the Table I it will be seen that in the case of coagulation of pure milk by HCl there are two zones of coagulation. One at a lower concentration (0.0067 M) and the other at a much higher concentration (0.168 M). It may be mentioned that coagulation of milk at the higher zone of coagulation was studied also by Dhar and coworkers.^{1,2}

After demarcating the two zones of coagulation with pure milk, experiments were repeated with the same milk diluted to different degrees by the addition of distilled water. The coagulation values obtained with HCl are give in Table II.

TABLE I
Coagulation of pure milk with HCl

No.	Milk	HCl	Water	Conc. of HCl in mixture (millimoles)	Results
1.	5 ml	3.0 ml of 0.02M HCl	2.0 ml	6.0	No Coagulation
2.	"	3.2 ml " "	1.8 ml	6.4	" "
3.	"	3.3 ml " "	1.7 ml	6.6	" "
4.	"	3.35ml " "	1.65 ml	6.7	Coagulated
5.	"	3.4 ml " "	1.6 ml	6.8	"
6.	"	3.5 ml " "	1.5 ml	7.0	"
7.	"	4.0 ml " "	1.0 ml	8.0	"
8.	"	5.0 ml " "	0.0 ml	10.0	"
9.	"	1.0 ml of 0.2M HCl	4.0 ml	20.0	"
10.	"	2.0 ml " "	3.0 ml	40.0	"
11.	"	2.5 ml " "	2.5 ml	50.0	"
12.	"	2.7 ml " "	2.3 ml	54.0	"
13.	"	2.8 ml " "	2.2 ml	56.0	"
14.	"	2.9 ml " "	2.1 ml	58.0	No coagulation
15.	"	3.0 ml " "	2.0 ml	60.0	" "
16.	"	4.0 ml " "	1.0 ml	80.0	" "
17.	"	2.5 ml of 0.4M HCl	2.5 ml	100.0	" "
18.	"	3.0 ml " "	2.0 ml	120.0	" "
19.	"	4.0 ml " "	1.0 ml	160.0	" "
20.	"	4.1 ml " "	0.9 ml	164.0	" "
21.	"	4.2 ml " "	0.8 ml	168.0	Coagulated
22.	"	4.3 ml " "	0.7 ml	172.0	" "
23.	"	4.5 ml " "	0.5 ml	180.0	" "
24.	"	5.0 ml " "	0.0 ml	200.0	" "

TABLE II
Coagulation of milk, pure and diluted with distilled water

Concentrations of Milk	Coagulation concentration in Millimol.	
	1st coag.	2nd coag.
Pure Milk	6.7	168
100 parts pure milk + 25 parts water	5.5	183
100 " " " + 50 parts "	5.0	191
100 " " " + 75 parts "	4.5	199
100 " " " + 100 parts "	4.1	204

From the above data it is clear that the ordinary dilution law: the lower the concentration of the colloid the smaller is the amount of the electrolyte necessary to coagulate : is applicable to the first zone of coagulation. But in the case of the second zone where higher concentration of electrolyte is necessary, a reverse that is, an abnormal rule is applicable.

A similar two separate zones of coagulation were observed with nitric, acetic, oxalic and tartaric acids and with chloride and nitrate of aluminium. An attempt was made to find out the nature of the dilution law applicable to the two zones in the case of these electrolytes. The two coagulation concentrations are given in Table III.

TABLE III
Coagulation values of milk pure and diluted with distilled water

Conc. of milk		Coagulation concentrations in millimol.											
		Nitric acid		Acetic acid		Oxalic acid		Tartaric acid		AlCl ₃		Al(NO ₃) ₃	
		1st coag.	2nd coag.	1st coag.	2nd coag.	1st coag.	2nd coag.	1st coag.	2nd coag.	1st coag.	2nd coag.	1st coag.	2nd coag.
Pure milk		6.2	80.8	6.5	†	9.57	329.0	3.44	†	4.2	66.0	3.4	*
100 parts milk	25 parts water	5.2	88.8	5.3	†	7.52	361.0	3.00	†	3.6	84.0	2.8	*
100 "	" 50 "	4.8	92.9	4.5	†	5.93	394.0	2.68	†	2.9	93.0	2.4	*
100 "	" 75 "	4.3	96.9	4.1	†	5.24	411.0	2.36	†	2.6	101.0	2.15	65.0
100 "	" 100 "	4.0	101.0	3.8	†	4.79	427.0	2.14	†	2.3	108.0	2.00	70.1

* :—At these dilutions the concentrations at which the charge reversal takes place and the concentrations at which the second coagulation takes place were so near that at times it was difficult to distinguish them.

† :—In this case the 2nd coagulation does not take place up to a concentration of 1 M.

In the following table III (a) are given the analysis of the different types of milks used.

TABLE III (a)

Milk	Fat content	Total Solid	Solid non fatty
Pure milk	4.6 %	13.5 %	8.9 %
Whole milk powder	2.7 %	11.8 %	9.1 %
Skimmed milk powder	0.1 %	9.1 %	9.0 %

It is apparent that the charge reversal with HCl , HNO_3 , CH_3COOH , oxalic and tartaric acid is due to the adsorption of H^+ ions and with AlCl_3 and $\text{Al}(\text{NO}_3)_3$ to the Al^{+++} ions and hence the milk which was negatively charged in the beginning should become positively charged on adsorption of these ions.

An attempt to find out if there is charge reversal with H_2SO_4 also failed to reveal any charge reversal. It was also found that with tartaric and acetic acids at all dilutions and with $\text{Al}(\text{NO}_3)_3$ at comparatively smaller dilutions it is not possible to distinguish the second zone of coagulation.

Coagulation experiments were carried out also with H_2SO_4 , AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{CH}_3\text{COO})_2$, CuSO_4 , ZnSO_4 , CoSO_4 , MnCl_2 , NiCl_2 and FeCl_3 . In these experiments the first coagulation zone was studied. The results obtained are given in Table IV. For the sake of comparison the results with HCl , HNO_3 , acetic, oxalic and tartaric acids together with AlCl_3 and $\text{Al}(\text{NO}_3)_3$ are also included.

In order to find out the effect of mixing natural milk with the whole milk powder and skimmed milk powder the coagulation of pure milk, liquified powder milk whole and liquified skimmed milk powder and the mixtures of these was studied. In order to have the results strictly comparable the coagulation of pure milk, liquified whole milk powder and powder skimmed milk diluted appropriately with distilled water were also studied by $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{CH}_3\text{COO})_2$, ZnSO_4 and AlCl_3 . The results are given in Tables V and VI.

TABLE IV

Coagulation of milk, pure, and diluted with distilled water by various electrolytes

Electrolytes	Coagulation concentrations in Millimol.				
	Pure milk	100 parts milk + 25 parts water	100 parts milk + 50 parts water	100 parts milk + 75 parts water	100 parts milk + 100 parts water
HCl	6.7	5.5	5.0	4.5	4.1
HNO ₃	6.2	5.2	4.8	4.3	4.0
CH ₃ COOH	6.5	5.3	4.5	4.1	3.8
Oxalic Acid	9.57	7.52	5.93	5.24	4.79
Tartaric Acid	3.44	3.00	2.68	2.36	2.14
H ₂ SO ₄	3.0	2.6	2.3	2.1	2.00
AgNO ₃	21.0	16.5	14.0	12.5	11.5
Pb(NO ₃) ₂	4.4	3.8	3.0	2.8	2.6
Pb(CH ₃ COO) ₂	4.0	3.4	3.0	2.6	2.4
CuSO ₄	8.6	6.8	6.0	5.1	4.4
ZnSO ₄	7.0	5.8	5.2	4.6	4.2
CoSO ₄	13.2	10.4	8.0	6.8	5.6
MnCl ₂	7.7	6.6	6.0	5.0	4.7
NiCl ₂	8.8	7.2	6.2	5.6	5.2
Al(NO ₃) ₃	4.2	3.6	2.9	2.6	2.3
AlCl ₃	4.2	3.6	2.9	2.6	2.3
FeCl ₃	5.6	4.6	4.0	3.6	3.1

TABLE V
Coagulation of milk pure and liquified powdered, whole and Skimmed

Electrolytes	Pure Milk	Whole milk powder	Skimmed milk powder	100 parts pure milk + 25 parts water	100 parts whole milk + 25 parts water	100 parts skimmed milk + 25 parts water	100 parts pure milk + 25 parts water	100 parts whole milk + 50 parts water	100 parts skimmed milk + 50 parts water	100 parts pure milk + 75 parts water	100 parts whole milk + 75 parts water	100 parts skimmed milk + 100 parts water	100 parts pure milk + 100 parts water	100 parts whole milk + 100 parts water	100 parts skimmed milk + 100 parts water
$\text{Pb}(\text{NO}_3)_2$	4.4	4.6	4.8	3.8	3.8	3.8	4.0	3.0	3.2	3.6	2.8	2.9	3.1	2.6	2.8
$\text{Pb}(\text{CH}_3\text{COO})_2$	4.0	4.2	4.4	3.4	3.5	3.6	3.6	3.0	3.1	3.2	2.6	2.8	2.4	2.4	2.5
ZnSO_4	7.9	7.3	7.5	5.8	5.9	6.4	5.2	5.2	5.6	4.6	4.7	4.8	4.2	4.3	4.4
AlCl_3	4.2	4.3	4.5	3.6	3.7	3.8	2.9	3.0	3.0	3.3	2.6	2.7	2.3	2.3	2.6

TABLE VI
Coagulation of mixtures of pure milk with liquified powdered milk both whole and skimmed

Electrolytes	Pure Milk	100 parts pure milk + 25 parts whole milk powder	100 parts pure milk + 50 parts whole milk powder	100 parts pure milk + 75 parts whole milk powder	100 parts pure milk + 100 parts whole milk powder	100 parts pure milk + 25 parts skimmed milk powder	100 parts pure milk + 50 parts skimmed milk powder	100 parts pure milk + 75 parts skimmed milk powder	100 parts pure milk + 100 parts skimmed milk powder
$\text{Pb}(\text{NO}_3)_2$	4.4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.6
$\text{Pb}(\text{CH}_3\text{COO})_2$	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.1	4.1
ZnSO_4	7.0	7.0	7.0	7.0	7.0	7.0	7.1	7.1	7.2
AlCl_3	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.3	4.3

In all these cases the normal dilution law is obeyed where only first zone of coagulation is determined. It will be interesting to note that powdered skimmed milk under practically identical conditions becomes more stable.

A point of interest is that H^+ from H_2SO_4 can not bring about the charge reversal probably due to the bivalency of the SO_4^{--} ions.

Previous workers have studied the coagulation of Prussian-Blue, gamboge, gum dammer, silver sol, milk, mastic, arsenious sulphide and antimony sulphide with various electrolytes. In the most of the cases reverse dilution law was obeyed with uni-univalent salts like KCl , KNO_3 , $NaOH$, CH_3COONa and KF . In some cases bi-univalent electrolytes such as $BaCl_2$, $CaCl_2$ and $Ba(NO_3)_2$ also showed abnormal dilution law, whereas electrolytes containing tri-valent Al^{+++} ions usually gave normal dilution law.

In this investigation we have observed that the same sol of milk which is negatively charged originally, follows normal dilution law but when charge reversal takes place it follows an abnormal law with HCl , HNO_3 , oxalic acid, $AlCl_3$ and $Al(NO_3)_3$.

An attempt to coagulate milk with bi-valent and tetra-valent ions with a view to find out as to the real cause of abnormal dilution law and its relation to the charge reversal is under investigation.

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INFLUENCE OF MOLASSES, PRESS-MUD AND CANE LEAF WITH AND WITHOUT PHOSPHATE (BONE MEAL) ON RECLAMATION OF SALINE AND ALKALINE SOILS

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ABSTRACT

Field trials in highly saline and alkaline soils of Bhupalsagar (Rajasthan) were conducted with eight treatments. Design of experiments followed was randomised block lay out and organic matter used were Molasses, Press mud and cane leaf alone and mixed with phosphate as Bone meal. Analysis of soil at different intervals showed a definite improvement in removal of salinity and alkalinity, salt concentration and in improving fertility status and the physical properties of the soils. Application of these organic matters or straw at the rate of ten tons and phosphate (P_2O_5) 100 lbs. per acre would prove a profitable and a permanent reclaiming agent for alkaline and highly saline soils of India and elsewhere.

Saline soils are unfit for cultivation of agricultural crops, pastures and forests, depending upon the concentration of the salts in soil solution. Gradually these soils become poorer in organic matter and tilth to still poorer condition due to high rate of oxidation of organic matter and leaching occurring in the soil. In humid and sub-humid climates a stage comes when these soils are converted into alkali soils. Saline soils are likely to become alkaline in canal irrigated areas also if a proper use of irrigation is not followed and drainage conditions are not satisfactory. In the Rajasthan State (India) the problem of soil salinity and alkalinity may become more acute on the introduction of canal irrigation and the problem has to be tackled from the very beginning. In countries like Hungary, Russia, Holland and the U. S. A. as well as in India use of chemicals like gypsum, sulphur or sulphuric acid for the reclamation of saline and alkali land has been practiced but as the humus status does not improve by these methods permanent reclamation of these soils may not be achieved. This is true for the soils of Rajasthan State which are already rich in the alkaline earth bases. Humus is a part of the soil exchange complex and acts as an excellent buffer in maintaining suitable soil reactions. There is an intimate relationship between the total phosphate status of the soil and its

humus content. Hence the phosphate content of the soil should be raised in order to raise the humus status.

Reclamation experiments in highly saline soils of *Bhupal Sagar* (Rajasthan) were carried out by the use of organic matter.

The organic matter like molasses, press-mud and cane leaf (which are easily available in the Sugarcane growing areas) were added to the saline soils for reclamation either alone or mixed with bone meal.

METHODS AND MATERIALS

Field trials were carried on in the Rawatia Farm of the Mewar Sugar Mills, Bhupalsagar situated two miles from the Bhupalsagar railway station. The sources of irrigation were canal and rain water. Several salt infected small and big patches of alkaline land are of common occurrence in this area and general morphology of the soil is black colour, hard, a thick layer of salt on the surface without any vegetation. The soil also forms cracks in the dry season and becomes very hard.

Lay out of the experimental plots was carried on 15th June, 1959. Molasses was diluted 10 times before it was applied to the plots. Cane leaf was thrashed on floor by bullock. Weighed quantity of amendments were applied and thoroughly mixed in the plots and moistened with water before the commencement of rains. Paddy was transplanted on 1st Aug., 1959 and harvested in the month of Nov., 1959 and barley was sown immediately afterwards. Barley crop was harvested in the month of April, 1960. Soil samples were collected and were analysed periodically. The analytical results have been recorded in the tables.

Analysis of the saturation extract of the soil was carried on by the method recorded in the U.S. Handbook No. 60 (22). The electrical conductivity was measured with the help of a 'Solubridge Soil Tester' (22), chloride by Mohr titration method using silver nitrate and potassium chromate, sulphate by gravimetric barium sulphate method, carbonate and bicarbonate by the method described by Ass. Off. Agric. Chemist 1950 p. 539, calcium by oxalate method, magnesium as magnesium pyrophosphate, potassium by the cobaltinitrite method (Piper 1942 p. 178), sodium as sodium uranyl magnesium acetate. pH was measured by a Beckman's pH meter using a glass electrode, mechanical analysis by pipette method (15). Methods used for determining the chemical composition, permeability, dispersion factor and water holding capacity are quoted by the reference numbers (29), (24), (19), (20). Exchangeable calcium was determined by Hissink's method (13), Ammoniacal and nitrate nitrogen by Olsen's method modified by Richardson (Piper 1942 p. 208), total nitrogen by Kjeldahl salicylic acid reduction method, organic carbon by the method of Robinson, Mclean and Williams (23), and available phosphate by Dyer's method (10).

Design of experiment :—

Randomised block layout.

Number of treatments : 8.

Number of replications : 4.

Number of plots : 32.

Area and size of the plot 1/60th of an acre, (33' × 22').

Rate of amendments per acre :

Organic matter 10 tons ; 100 lbs P_2O_5 as bone meal.

ANALYSIS OF THE SOILS UNDER FIELD TRIALS

Total analysis of the soil.

Moisture	—	2.1555 %
Loss on ignition	—	4.6051 %
Acid insoluble	—	70.3900 %
R_2O_3	—	13.3600 %
Fe_2O_3	—	5.5715 %
CaO	—	1.8744 %
MgO	—	1.1670 %
K_2O	—	1.3644 %
Na_2O	—	2.0826 %
P_2O_5	—	0.1334 %
Carbon	—	0.3920 %
Total nitrogen	—	0.1020 %

Mechanical composition of soil.

Coarse sand	—	20.00 %
Fine sand	—	27.60 %
Silt	—	27.20 %
Clay	—	17.25 %
Moisture	—	2.15 %
Loss due to solution	—	5.70 %

TABLE I

Analytical results of organic materials utilized

Composition		Cane leaf	Molasses	Press mud
Carbon	%	35.5434	23.2100	26.5000
Total nitrogen	%	1.4080	0.4111	3.3860
Moisture	%	8.0187	22.2756	4.9000
Loss on ignition	%	81.2000	65.5510	60.1400
Acid insoluble	%	7.9016	0.2243	13.2500
Sesquioxide	%	1.1694	0.1424	8.6000
CaO	%	0.9823	1.5652	6.8880
MgO	%	0.1426	0.7485	0.4528
K_2O	%	0.5432	4.4804	0.1155
P_2O_5	%	0.3405	0.1355	3.0880
Ash	%	10.7420	11.8213	34.9600
Sp. gr.	%	—	1.4283	—

TABLE No. 2

Analysis of saturation extract (Air dry basis)

Water soluble anions and cations in m.c./litre of saturation extracts

TREATMENT	Ca ⁺⁺	Mg ⁺⁺	Na ⁺⁺	K ⁺	HCO ₃ '	Cl'	SO ₄ ^H	Total cations Ob- tained	Cations calcula- ted**	Total anions
Original Analysis										
1. Control	...	178.00	64.27	1385.70	0.747	14.00	470.00	1144.72	1628.72	1328.72
2. Bone meal	...	184.00	63.04	1418.77	0.602	16.00	510.00	1140.42	1666.42	1366.42
3. Molasses	...	190.00	68.00	1329.64	0.774	12.00	480.00	1096.05	1588.42	1588.05
4. Molasses + B. M. (bone meal)	...	194.00	62.24	1229.18	0.820	16.00	486.00	984.24	1486.24	1486.24
5. Press mud	...	177.00	76.22	1392.83	0.599	18.00	504.00	1124.65	1646.65	1646.65
6. Press mud + B. M.	...	179.00	80.16	1207.74	0.726	15.60	480.00	972.02	1467.62	1467.62
7. Cane leaf	...	190.00	63.00	1344.58	0.480	14.00	196.00	1088.26	1598.26	1598.26
8. Cane leaf + B. M.	...	188.00	67.88	1332.06	0.624	12.60	476.00	1099.96	1588.56	1588.56

Analysis after 45 days of Treatments

1. Control	...	56.00	15.50	186.48	0.220	15.50	32.70	210.00	258.20	258.20
2. Bone meal	...	55.00	14.80	176.76	0.240	14.20	34.20	198.40	246.80	246.80
3. Molasses	...	50.00	16.20	164.96	0.220	16.70	32.00	184.70	229.98	229.98
4. Molasses + B. M.	...	48.00	15.00	161.50	0.200	15.00	37.70	176.00	224.70	224.70
5. Press mud	...	45.00	14.60	173.60	0.240	15.80	34.60	182.70	233.44	233.44
6. Press mud + B. M.	...	50.00	14.80	150.78	0.220	14.60	32.60	169.40	215.80	215.80

7. Cane leaf	...	48.00	14.40	161.46	0.240	16.40	33.80	174.00	224.10	207.9	224.10
8. Cane leaf + B. M.	...	52.00	15.00	149.20	0.200	15.20	33.60	167.60	216.40	196.0	216.40

Analysis after the Harvesting of Paddy Crop

1. Control	...	40.00	10.60	140.68	0.220	11.60	31.40	148.50	191.50	193.2	191.50
2. Bone meal	...	35.80	10.40	139.50	0.200	10.60	30.50	145.80	185.90	185.5	185.90
3. Molasses	...	10.40	3.70	44.67	0.140	6.20	12.60	40.20	58.91	52.6	59.00
4. Molasses + B. M.	...	10.20	4.20	42.36	0.040	5.40	11.40	40.00	56.80	51.4	56.80
5. Press mud	...	10.40	4.40	43.22	0.080	4.80	11.60	41.70	58.10	55.7	58.10
6. Press mud + B. M.	...	10.20	4.60	38.43	0.070	4.60	8.60	41.10	53.30	55.1	53.30
7. Cane leaf	...	14.20	4.20	38.24	0.160	5.60	10.70	40.50	56.80	52.6	56.80
8. Cane leaf + B. M.	...	15.70	4.70	38.12	0.080	4.80	12.00	41.80	58.60	51.4	58.60

Analysis after the Harvesting of Barley Crop

1. Control	...	24.60	6.20	89.40	0.200	8.22	22.47	89.71	120.40	120.40	120.40
2. Bone meal	...	22.20	5.20	86.20	0.140	8.05	22.22	83.47	113.74	113.60	113.74
3. Molasses	...	7.40	2.50	22.30	0.080	5.28	8.08	18.95	32.31	31.05	32.31
4. Molasses + B. M.	...	6.20	2.50	20.04	0.080	4.57	7.54	16.74	28.82	29.27	28.82
5. Press mud	...	6.60	2.20	20.20	0.060	4.20	8.21	16.65	29.06	28.68	29.06
6. Press mud + B. M.	...	6.50	2.00	20.00	0.040	4.20	8.05	16.29	28.54	27.54	28.54
7. Cane leaf	...	12.50	3.40	26.28	0.070	6.66	12.46	23.13	42.25	47.79	42.25
8. Cane leaf + B. M.	...	12.40	3.20	26.22	0.060	6.60	11.72	23.54	41.88	40.79	41.88

**10.37 × (E. C. × 10³)^{1.065}

TABLE No. 3

Changes taking place in Soil reaction (Saturation extracts) fertility status and physical properties of the Soil under field trials

TREATMENTS	pH	Electrical conduc- tivity E.C. X 10 ³	Analysis after mixing the amendments.					Ex-Ca m.e. %	W.H.C. † %	P ‡ cc/hr.	Dispersion factor %
			Org. C%	Total N%	C/N	Avail P ₂ O ₅ %					
			Original Analysis								
1. Control	...	7.90	95.0	0.3900	0.1020	3.8	0.1104	4.50	30.5	26.2	12.60
2. Bone meal	...	7.95	96.0	0.3903	0.1020	3.8	0.1114	4.50	30.5	26.5	12.55
3. Molasses	...	8.00	114.0	0.5939	0.1067	5.8	0.1116	4.60	32.2	28.2	11.92
4. Molasses + B. M.	...	8.00	107.0	0.5989	0.1067	5.8	0.1124	4.40	32.4	27.0	12.68
5. Press mud	...	8.00	118.0	0.6833	0.1401	4.8	0.1124	4.50	32.6	28.4	12.52
6. Press mud + B. M.	...	7.90	106.0	0.6833	0.1413	4.8	0.1126	4.50	32.0	29.0	12.50
7. Cane leaf	...	7.85	114.0	0.7830	0.1201	6.5	0.1116	4.50	32.0	28.4	11.85
8. Cane leaf + B. M.	...	7.85	113.0	0.7860	0.1194	6.5	0.1118	4.50	32.4	28.0	12.24

Analysis after 45 days of Treatments

1. Control	...	7.90	17.50	0.3920	0.1022	3.7	0.1040	6.60	30.5	26.2
2. Bone meal	...	7.90	16.80	0.3900	0.1024	3.8	0.1114	6.80	32.0	26.2
3. Molasses	...	7.70	16.50	0.5204	0.1132	4.6	0.1304	10.20	34.6	30.5
4. Molasses + B. M.	...	7.60	15.70	0.4842	0.1163	4.3	0.1412	10.50	38.2	32.5
5. Press mud	...	7.80	16.80	0.6300	0.1555	5.0	0.1774	10.40	40.0	36.0

6. Press mud + B. M.	...	7.70	14.60	0.6078	0.1564	5.9	0.1929	12.20	52.8	36.0	10.32
7. Cane leaf	...	7.80	16.70	0.6432	0.1227	6.9	0.1234	10.20	38.7	34.0	10.02
8. Cane leaf + B. M.	...	7.70	15.80	0.6806	0.1228	6.4	0.1238	10.30	39.0	34.0	10.50

Analysis after the Harvesting of Paddy Crop

1. Control	...	7.45	15.25	0.3150	0.1004	3.1	0.1024	6.80	30.0	25.0	13.74
2. Bone meal	...	7.04	15.00	0.3150	0.1006	3.1	0.1042	6.80	30.4	26.5	12.33
3. Molasses	...	7.28	4.60	0.4850	0.1220	3.9	0.1325	13.20	35.7	34.4	10.26
4. Molasses + B. M.	...	7.25	4.50	0.4520	0.1227	3.7	0.1426	13.70	36.0	35.0	10.24
5. Press mud	...	7.25	4.85	0.5550	0.1580	3.5	0.1648	14.20	42.5	40.5	9.84
6. Press mud + B. M.	...	7.25	4.80	0.5160	0.1566	3.3	0.1729	15.70	48.0	40.5	9.52
7. Cane leaf	...	7.30	4.60	0.7004	0.1283	5.4	0.1236	12.40	40.4	35.0	10.34
8. Cane leaf + B. M.	...	7.25	4.50	0.6420	0.1305	4.9	0.1307	13.80	40.5	35.0	10.26

Analysis after the Harvesting Barley Crop

1. Control	...	7.55	10.00	0.3150	0.1002	3.1	0.1025	6.40	30.4	26.0	12.54
2. Bone meal	...	7.50	9.48	0.3150	0.1005	3.1	0.1045	6.60	30.4	26.5	12.26
3. Molasses	...	7.30	2.80	0.4840	0.1223	3.9	0.1334	13.80	36.5	33.5	8.48
4. Molasses + B. M.	...	7.25	2.65	0.4440	0.1230	3.7	0.1445	14.60	39.2	33.8	8.23
5. Press mud	...	7.25	2.60	0.5232	0.1568	3.3	0.1528	15.60	44.2	40.2	7.22
6. Press mud + B. M.	...	7.20	2.50	0.4826	0.1647	2.9	0.1102	16.40	48.5	40.5	6.59
7. Cane leaf	...	7.40	4.20	0.5925	0.1324	4.4	0.1240	13.10	40.2	40.7	9.26
8. Cane leaf + B. M.	...	7.35	3.80	0.5232	0.1373	3.8	0.1309	14.00	40.2	40.8	9.24

† W. H. C. (Water Holding Capacity).

†† Permeability.

TABLE No. 4

Fluctuation in the quantities of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ during the growth period of paddy
and barley in the soil under field trials (mg/100 g soil)

Treatment	20th June 1959 before trans- planting paddy NH ₄ -N NO ₃ -N	6th Aug. 1959 after trans- planting paddy NH ₄ -N NO ₃ -N	30th Aug. 1959 after 3 weeks of transplanting paddy NH ₄ -N NO ₃ -N	20th Nov. 1959 after harvesting paddy crop NH ₄ -N NO ₃ -N	8th April, 1960 after harvesting barley crop NH ₄ -N NO ₃ -N						
Control	...	2.24	2.94	2.45	1.04	3.20	0.76	1.36	2.76	2.20	2.02
Bone meal	...	2.24	2.94	2.60	1.04	3.42	0.76	1.36	2.88	2.32	2.12
Molasses	...	2.24	2.94	3.54	1.48	4.56	1.22	2.14	3.96	2.46	2.86
Molasses + B.M.	...	2.24	2.94	3.67	1.78	4.87	1.42	2.45	4.46	2.46	2.92
Press mud	...	2.24	2.94	3.48	1.68	5.29	1.32	2.06	5.22	2.38	2.74
Press mud + B.M.	...	2.24	2.94	3.89	1.80	5.66	1.54	2.53	5.48	2.38	2.88
Cane leaf	...	2.24	2.94	3.42	1.20	4.20	0.82	1.80	4.08	2.40	2.14
Cane leaf + B.M.	...	2.24	2.94	3.44	1.27	4.32	0.89	1.80	4.20	2.42	2.28

TABLE No. 5
Yield of paddy grain in Kgm/acre

Treatments		B L O C K S				Total
		1	2	3	4	
1. Control	...	153.75	7.50	7.50	15.00	183.75
2. Bone meal	...	120.00	11.25	5.62	30.00	166.87
3. Molasses	...	157.50	120.00	90.00	157.50	525.00
4. Molasses + Bone meal	...	318.75	153.75	352.50	270.00	1095.00
5. Press-mud	...	405.00	311.25	517.00	247.50	1480.75
6. Press mud + Bone meal	...	517.75	630.00	543.75	315.00	2006.50
7. Cane leaf	...	153.75	41.25	45.00	35.00	275.00
8. Cane leaf + Bone meal	...	165.00	146.25	97.50	45.00	453.75
Total	...	1991.50	1421.25	1658.87	1115.00	6186.72 Grand total

TABLE No. 6
Analysis of variance of yield of paddy grains

Sources of variance		D. F.	S. S.	M. S.	F.	F.		Level of significance
						1%	5%	
Blocks	...	3	51566.4666	17188.8222				
Treatments	...	7	813038.2991	116148.3470	47.54	3.65	2.49	Very highly significant.
Error	...	21	51306.3592	2443.1571				
Total	...	31	915910.1149					

TABLE No. 7
Yield of paddy straw in Kgm/acre

Treatments		B L O C K S				Total
		1	2	3	4	
1. Control	...	255.00	22.50	15.00	60.00	352.50
2. Bone meal	...	210.00	18.75	26.25	112.50	367.50
3. Molasses	...	307.50	435.00	300.00	540.00	1582.50
4. Molasses + Bone meal	...	727.50	540.00	1016.25	900.00	3183.75
5. Press mud	...	885.00	900.00	1211.25	900.00	3896.25
6. Press mud + Bone meal	...	1320.00	1440.00	1485.00	1020.00	5265.00
7. Cane leaf	...	270.00	127.50	90.25	90.00	577.75
8. Cane leaf + Bone meal	...	285.00	405.00	330.00	86.25	1106.25
Total	...	4260.00	3888.75	4474.00	3708.75	16331.50 Grand total

TABLE No. 8
Analysis of variance of yield of paddy straw

Sources of variance	D. F.	S. S.	M. S.	F.	F.		Level of significance
					1%	5%	
Blocks	...	3	44628.7578	14876.2526			
Treatments	...	7	6004058.2422	857722.6060	42.28	3.65	2.49
Error	...	21	440878.6172	20994.2198			Very highly significant.
Total	...	31	6489565.6172				

TABLE No. 9
Yield of barley grains in Kgm./acre

Treatments	B L O C K S				Total
	A	B	C	D	
1. Control	90.00	90.00	120.00	75.00	375.00
2. Bone meal	112.50	90.00	150.00	90.00	442.00
3. Molasses	195.00	210.00	225.00	240.00	870.00
4. Molasses + Bone meal	240.00	270.00	270.00	390.00	1170.00
5. Press mud	360.00	270.00	195.00	240.00	1065.00
6. Press mud + Bone meal	390.00	525.00	240.00	375.00	1530.00
7. Cane leaf	165.00	135.00	150.00	135.00	585.00
8. Cane leaf + Bone meal	180.00	195.00	210.00	195.00	780.00
	1732.50	1785.00	1560.00	1740.00	6817.50

TABLE No. 10
Analysis of variance of yield data of Barley grains

Sources of variance	D. F.	S. S.	M. S. S.	F.	Expected value of F at	
					1 %	5 %
Blocks	...	3	3675.5862	1225.1954		
Treatments	...	7	269548.2425	38506.8917	11.16**	3.66
Error	...	21	70560.3513	3360.0170		2.49
Total	...	31	343784.1800			

** Highly significant.

TABLE No. 11
Yield of Barley straw in Kgm/acre

Treatments		B L O C K S				Total
		A	B	C	D	
1. Control	...	150.00	180.00	150.00	105.00	585.00
2. Bone meal	...	202.50	195.00	210.00	120.00	727.50
3. Molasses	...	255.00	210.00	255.00	360.00	1080.00
4. Molasses + Bone meal	...	258.75	300.00	270.00	540.00	1368.75
5. Press mud	...	420.00	240.00	247.50	240.00	1147.50
6. Press mud + Bone meal	...	435.00	480.00	300.00	375.00	1590.00
7. Cane leaf	...	180.00	225.00	150.00	165.00	720.00
8. Cane leaf + Bone meal	...	225.00	255.00	225.00	225.00	930.00
Total	...	2126.25	2085.00	1807.50	2130.00	8148.75

TABLE No. 12
Analysis of variance of yield data of barley straw

Sources of variance		D. F.	S. S.	M. S. S.	F.	Expected value of F at	
						1 %	5 %
Blocks	...	3	8948.5840	2982.8613			
Treatments	...	7	209812.0605	29973.1515	5.72**	3.65	2.49
Error	...	21	110086.9630	5242.2363			
Total	—	31	329847.6075				

RESULTS AND DISCUSSION

The changes that took place in the soil solution, soil reaction, physical properties and the fertility status of the soil under field experiment during the growing season of Paddy and Barley are recorded in tables Nos. 2 and 3. These results indicate that the soil under field trials is highly saline and appreciably alkaline. Values obtained for total soluble anions and cations and electrical conductivity are very high. Amongst the cations sodium ions are dominating, while sulphate and chloride ions are dominating anions. Bicarbonate ions are present in small quantity while carbonate ions are practically absent. This is to be expected as the pH of the soil did not exceed 8.

Analysis of the soil samples taken after 45 days of treatments i.e. just before transplanting of Paddy, soil samples taken after the harvesting of Paddy and Barley crops show that there is marked decrease in the soluble cations and anions, electrical conductivity and pH values. In general the organic matter mixed with

** Very highly significant.

phosphate (bone meal) is more efficient in removing the salts and lowering the pH and the electrical conductivity values. The effect of different treatment in lowering these values is of the following order.

Press mud + Bone meal > Molasses + Bone meal > Press mud >

Molasses > Cane leaf + Bone meal > Cane leaf > Bone meal > Control.

These results also indicate that in porous soils leaching is effective in removing the salts to a limited extent and becomes ineffective in removing the salts adsorbed on the exchange complex of the soil. Decrease in the pH value and lowering of salt concentration may be attributed to the fact that during the oxidation of organic matter, carbonic acid and certain other acids are liberated and they acid in lowering the pH value, soil is flocculated and thus leaching is enhanced.

The relationship between total soluble cations and the electrical conductivity was found to be correlated. Correlation coefficient was calculated between the logarithm of total soluble cations and the logarithm of electrical conductivity and was found to be $r = 0.8156$, which is highly significant at 0.1 % level of significance. There is positive correlation, i.e. the increase or decrease in the value of total soluble cations follows the increase or decrease in the respective values of the electrical conductivity.

Total soluble cations of the saturation extracts of the soil samples have been compared with the figures obtained by calculating them according to the equation proposed by Campbell et al (5).

T. S. C. (total soluble cation) in milliequivalent per litre = $10.37 (E.C. \times 10^3) 1.065$.

These calculated and observed values closely approximate each other. Banerjee (3) observed a significant correlation between log of T. S. C. and log of electrical conductivity in the salt infected soils of West Bengal (India). Fireman and Reeve (12), describing the characteristics of saline and alkali soils in the U. S. A., reported excellent relationship between T. S. C. determined by chemical analysis and E. C. of saturation extract of the soil.

Analysis of the soil samples taken at different intervals for organic carbon, total nitrogen, available phosphate, exchangeable calcium water holding capacity, dispersion factor and permeability are recorded in table No. 3. There is a considerable increase in the amount of total nitrogen, available phosphate and exchangeable calcium on treatment and this increase is of the following order.

Press mud + Bone meal > Press mud > Molasses + Bone meal >

Molasses > Cane leaf + Bone meal > Cane leaf > Bone meal > Control.

Singh and Nijhawan (25) Breazeale and McGeorge (2) Singh and Nijhawan (26) (27) Basu and Tagore (4) observed considerable increase in these values by the application of Farm yard manure in alkali and calcareous alkaline soils. Their findings confirm that the abundant supply of CO_2 and organic acid on the oxidation of organic manures aids in increasing available P_2O_5 and exchangeable calcium.

The results also indicate an increase in the water holding capacity and permeability and decrease in dispersion factor by the application of these amendments as the effect of Na ions on the soil colloids is restored to normal conditions by Ca ions.

The results shown in table No. 4 indicate that during the early growth period *i.e.* in the third week after the transplantation of Paddy, the amount of ammoniacal nitrogen was greater than that of nitrate nitrogen, while reverse was noted in the later stages *i.e.* after the harvesting of Paddy and Barley. The above observations indicate that Paddy crop is able to utilise ammoniacal form of nitrogen and the presence of greater amount of $\text{NH}_4 - \text{N}$ may be attributed to the fact that under water logged condition in soil, the reduction process may dominate the oxidation process, thus the formation of $\text{NO}_3 - \text{N}$ is slowed down. Dastur and Malkani (7) have shown that the absorption of ammonia by rice plants is greater in the early stages and then it becomes slower while the absorption of NO_3 ions becomes greater as the plant ages. Arrhenius (1) Ellis and Morrison (11) observed more ammonia in acidic condition and more nitrate under alkaline condition in soils. Russell (21) observed more $\text{NH}_4 - \text{N}$ in manured soils as compared to unmanured ones. Subramanayan (28) found an increase in the ammonia content in water logged soils. Dhar and Mukerji (8) Dhar and Gopala Rao (9) made a systematic study on the process of ammonification and nitrification and established that these processes may be purely photochemical and surface reactions. Mirchandani (17) observed definite improvement in the nitrogen content by adding molasses and sugar cane trash compost to soil.

The yield data of Paddy grains and straw are given in table Nos. 5 and 7 respectively. The average yield of Paddy grains and straw in each block for each treatment show to bear a definite ratio and this ratio comes to 1 : 2 in general. The efficiency of different treatments in increasing the yield of paddy grains and straw is as follows :—

Press mud + Bone meal > Press mud > Molasses + Bone meal >

Molasses > Cane leaf + Bone meal > Cane leaf > Bone meal > Control.

Analysis of variance of yield of Paddy grains and straw is given in table Nos. 6 and 8. The results show that the calculated F values for grains and straw are very highly significant at 1 % and 5 % level of significance and that there is significant difference between the yields in different treatments.

The yield data of barley grains and straw are recorded in tables Nos. 9 and 11. In this case the ratio of grains and straw is 1 : 1 and the order of efficiency of different treatments in increasing the yield of grains and straw is the same as noted in the case of paddy crop. Analysis of variance of yield of barley grains and straw is shown in table Nos. 10 and 12. The calculated F values obtained for both grain and straw are highly significant at 1 % as well as 5 % level of significance for different treatments.

These results of yield data obtained in the present investigations show that in the process of reclamation of saline and alkaline land, growing of Paddy crop followed by Barley is very effective. Henderson (14) Mann and Tamhne and (16) Puri (18) observed that growing of Paddy and Barley crops is profitable in reclaimed soils.

From the foregoing observations it appears that saline and alkaline land can be reclaimed successfully by the application of organic substances mixed with phosphates.

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STUDY OF THE PRODUCTS FORMED BY THE OXIDATION OF MERCUROUS NITRATE BY POTASSIUM PERSULPHATE

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ABSTRACT

The nature of the reaction product precipitating out during the oxidation of mercurous nitrate by potassium persulphate in nitric acid medium has been investigated. At low concentration of nitric acid, the final product separating out is lemon yellow in colour and is basic mercuric sulphate, $\text{HgSO}_4 \cdot 2\text{HgO}$. On increasing the concentration of $\text{Hg}_2(\text{NO}_3)_2$, the lemon yellow precipitate becomes contaminated with white Hg_2SO_4 due to the precipitation of Hg_2^{++} by SO_4^{--} formed by the reduction of $\text{K}_2\text{S}_2\text{O}_8$. The initial product formed is white HgSO_4 which changes to a lemon yellow basic salt $\text{HgSO}_4 \cdot 2\text{HgO}$ on standing in aqueous solution. At high concentration (0.96N) of nitric acid, the precipitate is white and is Hg_2SO_4 , the mercuric sulphate being soluble at this concentration of nitric acid. The above conclusions have been confirmed by qualitative and quantitative analysis of the different precipitates.

During the kinetic study of oxidation of mercurous ion by persulphate ion, it was observed by us that under certain conditions, a precipitate separated out during the course of reaction, and further that the physical state of the precipitate was different under different conditions. The present study was undertaken with a view to determine the conditions under which precipitate formation takes place and to investigate the physical and chemical properties of these precipitates.

It may be pointed out that a reference to literature shows that no study has been made of the oxidation of mercurous ion by persulphate ion. However, the oxidation of metallic mercury into yellow mercuric oxide or basic mercuric sulphate has been reported by Levi, Migliorini and ErColini (1). The formation of the oxysalt $\text{HgSO}_4 \cdot 2\text{HgO}$ by the oxidation of metallic mercury by sodium persulphate is also shown by Montignie (2).

EXPERIMENTAL

Mercurous nitrate and potassium persulphate of G. R., E. Merck quality and nitric acid, A. R., B. C. P. W. quality have been used throughout the course of the work. All other reagents used were also of A. R. quality. For studies on precipitate formation by the oxidation of mercurous ion, a definite volume of potassium persulphate was taken in glass stoppered pyrex conical flask, to this a known concentration of concentrated nitric acid and the required weight of solid mercurous nitrate was added, and the solution was shaken to dissolve the mercurous nitrate. The flask was then allowed to stand for precipitate formation during oxidation. During the course of the present investigation, it was found that precipitation is quicker when the temperature was about 60–70°C. Hence, in the later work for the preparation of oxidation products for chemical analysis, the precipitation was carried out by keeping the flasks at 60–70°C.

The precipitates in different experiments were filtered through buchner funnel and washed with boiling water in preliminary experiments. It was found that during washing with hot water, some of the particles change to grey colour in the

case of yellow precipitates while in the case of white precipitates the whole of the precipitate changes to dirty green colour. Hence, in later work the yellow precipitate was first washed with warm water containing few drops of nitric acid and finally with warm water alone till free from mercurous ions. The white precipitate was first washed with warm water containing few drops of dilute sulphuric acid to remove mercurous ion and followed by one or two washings with water alone. The above methods of washing were adopted in order to prevent the change in colour of the precipitate. It may be mentioned that it has been reported by Gouy (3) that the change of mercurous sulphate into basic salt by the action of water is prevented if water contains 0.08 gm. of sulphuric acid per liter.

The precipitates after proper washing were dried in the oven first at 60°C and then at 140°C. It was found that there was no change in the weight of the precipitate after heating at 140°C. showing that the precipitate does not contain any water of crystallisation. Therefore, in the present investigation, the precipitates were always dried in an oven at about 140°C to constant weight.

Qualitative tests for the different constituents present in the precipitate were carried out by dissolving the precipitate in minimum concentration of nitric acid in the following manner :—

- (i) Mercurous ion was tested with NaCl solution.
- (ii) Mercurous ion was precipitated completely with NaCl solution and removed by centrifuging and the centrifuged liquid was tested for the presence of mercuric ions with the help of H_2S and $SnCl_2$. Spot test for mercuric ion with cobalt acetate solution was also carried out.
- (iii) The presence of sulphate ion was detected with the help of $BaCl_2$ solution in the centrifuged liquid. The test for sulphate ion was also carried out with $Ba(NO_3)_2$ solution and sodium rhodizonate solution in the original liquid.

Quantitative estimation of mercurous ion was carried out gravimetrically by precipitation with NaCl solution as recommended by Schmidt (4). For the estimation of mercuric ion, first the solution in dilute nitric acid was taken and mercurous ion was removed by precipitation with NaCl solution, centrifuging and then mercuric ion precipitated as mercuric sulphide with H_2S . The precipitate was washed successively with small amounts of carbon disulphide, alcohol and ether to remove any sulphur formed. Mercuric ion was also estimated by shaking the precipitate with 50% HCl to dissolve the mercuric salt alone, diluting with water and centrifuging the solution to remove mercurous, and then precipitating mercuric in the centrifuged liquid with H_2S . The amount of sulphate present in the precipitate was estimated by taking the solution in nitric acid and precipitating sulphate as $BaSO_4$ with $Ba(NO_3)_2$ solution. It was also estimated by precipitation with $BaCl_2$ solution in the centrifuged liquid when the precipitate was shaken with fifty percent HCl (free of mercurous ion). Since the results obtained by the use of sintered crucibles were found to be high, the final estimations were carried out in silica crucibles.

QUALITATIVE OBSERVATIONS

Preliminary experiments showed that the oxidation product of mercurous nitrate with potassium persulphate does not precipitate out at very low concentration of the reactants and at high concentration of nitric acid. Hence, in

the first series of experiments the conditions under which the oxidation products precipitate out were determined. The observations in this series of experiments are summarised below.

TABLE I
Effect of reactants and nitric acid concentration.

Expt. No.	Overall conc. of $K_2S_2O_8$	Overall conc. of $Hg_2(NO_3)_2$	Overall conc. of HNO_3	Observations.
1.	0.01 N	0.01 N	0.8 N	No formation of ppt. even on keeping for three days at room temperature
2.	0.01 N	0.01 N	0.48 N	Very small amount of lemon yellow crystalline ppt. on standing.
3.	0.1 N	0.1 N	0.8 N	No formation of ppt.
4.	0.1 N	0.1 N	0.48 N	Very small amount of dirty white ppt.
5.	0.5 N	0.525 N	0.16 N	Large amount of white needle shaped ppt. formation next day, changing to yellow on standing.
6.	"	"	0.32 N	Heavy precipitation of white coloured ppt. next day, changing to yellow on standing.
7.	"	"	0.40 N	" " "
8.	"	"	0.8 N	White crystalline ppt. next day, changing to dirty white on standing.
9.	"	"	1.6 N	Round shaped white crystalline ppt. after 24 hours.
10.	"	"	4.8 N	Practically no ppt. formation even after standing for 72 hours.

From the above experiments it is seen that at very low concentration (0.01 N) of the reactants and at moderately high concentration of nitric acid (0.8 N), the precipitate formation of the oxidation product does not take place. Further, it is seen that slight precipitate formation does take place in dilute solutions of the reactants when the concentration of nitric acid is low. The increase in concentration of nitric acid in the case of moderately high concentration of the reactants (0.5 N) not only brings about a change in the amount of the precipitate separating out, but also in the physical state of the oxidation product formed. Thus, in the case of white precipitate the size of the particles increases with an increase in the concentration of HNO_3 .

In the next series of experiments, the effect of variation in the concentration of the reactants, particularly that of mercurous nitrate at constant nitric acid

concentration was studied. In the first set, the concentration of HNO_3 was kept constant at 0.16 N and that of potassium persulphate at 0.5 N while the concentration of mercurous nitrate was varied from 0.13 N to 0.5 N in six experiments. It was found that in each case the final colour of the precipitate formed was yellow. Further, as the concentration of mercurous is increased, the amount of the precipitate formed also increases. In the next set, the concentration of HNO_3 was increased to about 1 N and the concentration of mercurous nitrate was varied from 0.18 N to 0.5 N at 0.5 N potassium persulphate concentration. In this case, it was found that the final colour of the precipitate formed was always white. Here also, the amount of precipitate increases with an increase in mercurous nitrate concentration.

CHEMICAL ANALYSIS OF THE PRODUCTS

As indicated in the experimental part, the presence of mercurous, mercuric and sulphate in the yellow and the white products was carried out by conventional methods and the following results were obtained.

TABLE 2
 $\text{K}_2\text{S}_2\text{O}_8 - 0.5 \text{ N}$

Expt. No.	$\text{Hg}_2(\text{NO}_3)_2$ conc. taken	HNO_3 conc. used	Radicals present
Yellow product :			
1.	0.13 N	0.16 N	$\text{Hg}^{++}, \text{SO}_4^{--}$
2.	0.18 N	"	$\text{Hg}^{++}, \text{SO}_4^{--}$, negligible amount of mercurous.
3, 4, 5, & 6	0.26, 0.36, 0.435, 0.5 N	"	$\text{Hg}^{++}, \text{Hg}_2^{++}, \text{SO}_4^{--}$
White product :			
7.	0.18 N	0.96 N	$\text{Hg}_2^{++}, \text{SO}_4^{--}$
8, 9, 10, & 11	0.26, 0.36, 0.5 N, 0.435 N	"	$\text{Hg}^{++}, \text{Hg}_2^{++}, \text{SO}_4^{--}$ $\text{Hg}_3^{++}, \text{SO}_4^{--}$ (directly kept in oven at 60–70°C.).

The oxidation of mercurous nitrate with potassium persulphate in experiments no. 7, 8, 9 and 10 were carried out by keeping the mixture of the two solution at room temperature overnight, while in experiment no. 11 it was carried out by keeping the mixture of solutions at 60–70°C. for about three hours. It was observed that the product formed in experiments 8–10 is not appreciably soluble even in 10–15% of HNO_3 and therefore the solution for chemical analysis had to be prepared in hot 50–60% HNO_3 while the precipitates in experiments 7 and 11 are

soluble in 10-15% HNO_3 in cold. Hence, the presence of mercuric in the white product in experiments 8, 9, and 10 is possibly due to the oxidation of mercurous by concentrated nitric acid during the process of dissolution.

Further, it is seen that in the case of yellow product, there is no mercurous present in the precipitate when the concentration of mercurous nitrate taken in 0.13 N but on increasing its concentration, mercurous starts appearing at 0.18 N concentration of mercurous nitrate and the amount of mercurous present in the precipitate increases with further increase of mercurous nitrate.

QUANTITATIVE ANALYSIS

The lemon yellow as well as the white precipitates obtained were quantitatively analysed for mercurous mercury, mercuric mercury and sulphates present, by methods already mentioned in the experimental details. The results are summarised in Table 3:

TABLE 3

Results of quantitative analysis of dried precipitates.

Precipitate	Estimated	Probable formula	%Hg		%SO ₄	
			Exptal	Theory	Exptal	Theory
(a) Lemon yellow Table 2, Expt. 1	Hg (ic) as HgS and SO ₄ as BaSO ₄	HgSO ₄ . 2HgO	82.3	82.5	13.13	13.16
(b) White Table 2, Expt. 11	Hg (ous) as Hg ₂ Cl ₂ and SO ₄ as BaSO ₄	Hg ₂ SO ₄	80.0	80.5	19.6*	19.3
(c) Lemon yellow Table 2, Expt. 5	Hg (ous) as Hg ₂ Cl ₂ and Hg (ic) as HgS and SO ₄ as BaSO ₄	Mixt. of Hg ₂ SO ₄ and HgSO ₄ 2HgO	%Hg ₂ SO ₄ (Exptal) 3.3	% of HgSO ₄ .2HgO (Exptal) 96.1	Estimated Total %	99.4

From the above results it is evident that the lemon yellow precipitate (a) has the composition $\text{HgSO}_4 \cdot 2\text{HgO}$, while (c) is a mixture of Hg_2SO_4 and $\text{HgSO}_4 \cdot 2\text{HgO}$ the ratio of which was found to vary in different experiments. The white precipitate (b) appears to be Hg_2SO_4 .

CONCLUSION

From the above observations it is concluded that two compounds probably precipitate out when a solution of mercurous nitrate in HNO_3 and $\text{K}_2\text{S}_2\text{O}_8$ are mixed

* 2% high results may be due to barium nitrate present in soln.

together and allowed to stand. At low concentrations of HNO_3 and low concentration of $\text{Hg}_2(\text{NO}_3)_2$ the substance precipitating out is a basic mercuric salt, probably of the formula $\text{HgSO}_4 \cdot 2\text{HgO}$. The above conclusion is borne out by the physical nature of the precipitate (lemon yellow colour) *cf.* the observations of Ray on $\text{HgSO}_4 \cdot 2\text{HgO}$ (5)] and the effect of heat [*cf.* the observations of Watson ; (6) ; Houston (7) ; Hildebrandt (8) and Ray on $\text{HgSO}_4 \cdot 2\text{HgO}$]. Further, it may be mentioned that the precipitate formed is always white in the beginning which changes to yellow on standing in aqueous medium. This suggests that on oxidation, first mercuric sulphate is formed according to the over all reaction $\text{K}_2\text{S}_2\text{O}_8 + \text{Hg}_2(\text{NO}_3)_2 = 2\text{HgSO}_4 + 2\text{KNO}_3$ which changes into the lemon yellow basic salt on contact with water [*cf.* observations of Phillips on HgSO_4 (9)]. At low concentrations of HNO_3 and higher concentrations of $\text{Hg}_2(\text{NO}_3)_2$, the precipitate is probably a mixture of Hg_2SO_4 and $\text{HgSO}_4 \cdot 2\text{HgO}$. In both of these cases the product is lemon yellow in colour. The fact that some particles change into dirty green colour on washing with boiling water suggest that this is due to the presence of small amounts of Hg_2SO_4 as confirmed by quantitative analysis. However, at higher concentrations of HNO_3 the product separating out is white and is Hg_2SO_4 , the mercuric salt formed on oxidation being probably soluble in the high concentration of HNO_3 employed. This conclusion is corroborated by the physical nature, the effect of washing and light [*cf.* the observations of Gouy (*loc. cit*) and of Hada (10)] and the effect of heat [*cf.* the observations of Gay Lussac on Hg_2SO_4 (11)] on the white product.

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SOME MIXED ORTHOFORMIC ESTERS: REACTIONS OF ETHYL ORTHOFORMATE WITH TERTIARY BUTYL ALCOHOL

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ABSTRACT

The mixed orthoformic esters of tertiary butyl alcohol have been prepared by alcohol interchange technique using a mixture of anhydrous aluminium chloride and anhydrous zinc chloride as catalysts. The compounds prepared are tertiary butyl diethyl orthoformate and ditertiary butyl ethyl orthoformate.

The orthoformic esters are chemically unique materials, closely resembling acetals, stable to alkali but unstable to aqueous acids and their various reactions have proved to be a powerful tool in synthetic organic chemistry, because they are important in the synthesis of vitamin B complex, antimalarials, special polymers and are extensively used in the field of cancer research.

In view of above, reactions of alkyl orthoformates in organic synthesis have attracted considerable attention recently and various orthoformic esters have been prepared. Alexander and Busch¹ prepared several high-boiling orthoformates starting from ethyl orthoformate using alcohol interchange technique.

These workers also attempted the preparation of isopropyl and tertiary butyl orthoformates by the trans-esterification of ethyl orthoformate, but in each case the interchange did not occur. Later Roberts et al² however succeeded in preparing isopropyl orthoformate starting from methyl orthoformate and reported that interchange was quite slow. The addition of a small amount of concentrated sulphuric acid markedly increased the rate of removal of methyl alcohol and obtained isopropyl orthoformate in 75% yield. They also emphasised the advantages of the use of acid catalysis in the trans-esterification of ethyl alcohol by all primary and low-boiling secondary alcohols. But they failed to effect the interchange between methyl orthoformate and tertiary butyl alcohol using acid catalysis. The acid employed first dehydrated the tertiary alcohol and later hydrolysed the orthoester. In the absence of acid catalysis no reaction occurred by heating the reactants even to 48 hours or longer. However by the use of small amounts of metallic sodium, there was no dehydration, but the alcohol was liberated very slowly. For reaction with high-boiling secondary alcohols, they recommended the use of acid catalysis with simultaneous removal of the alcohol.

Thus it appears that the reaction between alkyl orthoformate and tertiary butyl alcohol has not been successful so far and even mixed tertiary ortho-esters have not been reported.

Attempts were made to bring about the trans-esterification between $\text{HC}(\text{OC}_2\text{H}_5)_3$ and $(\text{CH}_3)_3\text{COH}$ in boiling benzene and fractionating out the benzene-ethanol azeotrope continuously, over long periods, as it was formed. It was found

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that simply by refluxing the above two in benzene under a column, or by refluxing in presence of a little metallic sodium and then removing the benzene-alcohol azeotrope gave negative results for ethanol in the azeotrope showing that the metallic sodium did not catalyse the reaction and no ethanol was formed in the reaction. Thus these observations seem to confirm the results of earlier investigators. However, the reaction is possible when it is catalysed by a mixture of a little anhydrous AlCl_3 and ZnCl_2 . Afterwards distillation of the compound under reduced pressure gave tertiary butyl diethyl orthoformate and ditertiary butyl ethyl orthoformate. The third ethoxy group could not be replaced by tertiary butoxy. It was, however, noted that if instead of taking a mixture of the above two solid catalysts, when only anhydrous AlCl_3 was used, the ethanol liberated in the azeotrope was less than the theoretical amount required for replacement. Thus the presence of anhydrous ZnCl_2 was found to be always helpful in these interchange reactions.

Further, in order to confirm that no dehydration of the alcohol was taking place which might give rise to butylenes and which might have reduced the chromic acid used in the estimation of azeotrope, a blank experiment was done in identical conditions using only $(\text{CH}_3)_3\text{COH}$ and C_6H_6 and refluxing with a mixture of anhydrous AlCl_3 and ZnCl_2 and fractionating out the azeotrope over long periods, showed no reduction of chromic acid in the azeotrope, thereby confirming that no butylene was coming in the azeotrope.

The formation of tert. butyl diethyl orthoformate and di tert. butyl ethyl orthoformate shows that as the ethoxy groups are successively replaced by tertiary butoxy, the latter goes on shielding the molecule so much so that they render the third ethoxy group incapable of displacement and so tertiary butyl orthoformate does not appear to be possible by the alcohol interchange technique.

EXPERIMENTAL

Apparatus : All glass apparatus with interchangeable joints was used throughout and special precautions were taken, to exclude moisture. Fractionations were carried out in a column packed with Raschig rings and fitted to a total condensation variable take-off stillhead.

Materials :

Ethyl orthoformate : was prepared by Williamson's method and redistilled before use. The fraction taken was between $145-148^\circ\text{C}$.

Tertiary butyl alcohol : was dried over metallic sodium and freshly distilled.

Benzene : was dried by storage over sodium wire and finally dried azeotropically with alcohol over a long column.

Analytical Method : The ethoxy content was estimated by the method described by Bradley, Halim and Wardlaw³. A little weighed substance was taken in a special small bottle to which was added a measured amount (excess) of standard chromic acid and after allowing to stand for about two hours at the room temperature, the unused chromic acid was titrated iodometrically.

(a) Reaction between $\text{HC}(\text{OC}_2\text{H}_5)_3$ and $(\text{CH}_3)_3\text{COH}$ in dry benzene (Molar ratio: 4:4).

To ethyl orthoformate (4.90 g.) was added dry tertiary butanol (10.93 g.) and benzene (68.32 g.). After refluxing the mixture at about 12°C for about two hours, it was carefully fractionated out into two parts. The first fraction (28.02 g.) was collected upto 73°C while the second (50.0 g.) was collected between 73 and 80°C. Analysis of both the fractions showed no ethanol.

The liquid remaining in the flask was distilled out, when a colourless liquid (4.0 g.) was obtained at about 145°C which had ethoxy 91.20% (Calc. for $\text{HC}(\text{OC}_2\text{H}_5)_3$; ethoxy 91.21%).

(b) Reaction between $\text{HC}(\text{OC}_2\text{H}_5)_3$ and $(\text{CH}_3)_3\text{COH}$ in benzene in presence of a little metallic sodium (Molar ratio 1 : 6.9).

To ethyl orthoformate (4.23 g.) was added dry tertiary butanol (14.4 g.) and benzene (50.0 g.) and then a small piece of dry metallic sodium (0.3 g.). After refluxing the contents for 2 hours at 115°C, about 9.9 g. was fractionated out at 73.5° and about 50 g. between 74 and 80°C, both collected in course of about 8 hours. Analyses of both these showed no ethanol.

(c) Reaction between $\text{HC}(\text{OC}_2\text{H}_5)_3$ and $(\text{CH}_3)_3\text{COH}$ in benzene in presence of a little anhydrous AlCl_3 and a little anhydrous ZnCl_2 . (Molar ratio 1:4.6).

To ethyl orthoformate (18.61 g.) was added dry tertiary butanol (42.70 g.) and benzene (60.0 g.) To the mixture was then added anhydrous AlCl_3 (0.5 g.) and anhydrous ZnCl_2 (0.2 g.) After refluxing the whole for 10 hours (bath temp. 115-120°) about 81.5 g. of the azeotrope was fractionated out at 72°C (bath temp. 115-160°) in course of about 2 days.

Total ethanol in the azeotrope = 4.44 g.

Theoretical ethanol required for one interchange = 5.77 g. The liquid remaining (34.0 g.) after removal of the azeotrope was treated with a little dry benzene (about 10 c. c.) and quickly filtered through the pump. Then it was subjected to reduced pressure distillation when a colourless liquid (8.0 g.) was obtained at 57 - 59°/13 - 14 m.m. (Found : $\text{C}_2\text{H}_5\text{O}$, 51.02, 51.00 ; Calc. for $(\text{C}_2\text{H}_5\text{O})_2\text{CH}(\text{OC}_2\text{H}_5)_2$, $\text{C}_2\text{H}_5\text{O}$ 51.13%)

(d) To ethyl orthoformate (15.38 g., 1 mol) was added dry tert. butanol (37.04 g., 4.8 moles) and benzene (55.0 g.). To this mixture was then added anhydrous AlCl_3 (0.3 g.) and anhydrous ZnCl_2 (0.2 g.). After refluxing the whole for about 18 hours (bath temp. 115 - 120°), about 3 g. of an azeotrope was fractionated out between 66-67.5° and then 73.72 g. between 67.5 - 72°; in course of about 2½ days. Fractionation was stopped a little before completion.

Total ethanol from both azeotropes = 7.937 g.

Theoretical ethanol required for two interchanges 9.56 g.

The liquid remaining (25 g.) after removal of the azeotrope was quickly filtered through the pump and washed with about 10 c. c. dry benzene. After removal of benzene at the pump, when reduced pressure distillation was restored to, a colourless liquid (7.0 g.) was obtained at 33 - 35°/10 - 12 m.m. (Found : $\text{C}_2\text{H}_5\text{O}$, 22.5, 22.4 ; Calc. for $(\text{C}_2\text{H}_5\text{O})_2\text{CH}(\text{OC}_2\text{H}_5)_2$, $\text{C}_2\text{H}_5\text{O}$, 22.05%)

Blank experiment using only $(CH_3)_3COH$ and dry benzene under above identical conditions. Dry benzene (25.49 g.) was added to dry tert. butanol (15.51 g.), to which was then added anhydrous $AlCl_3$ (0.4 g.) and anhydrous $ZnCl_2$ (0.2 g.). After refluxing the whole for about 18 hours, a colourless liquid (35.0 gm.) was fractionated out between 69.5° and $71.5^\circ C$ in course of about 10 hours. This was treated with standard chromic acid, when no reduction took place.

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ADSORPTION OF FLUORESCEIN ON HYDROUS MOLYBDIC OXIDE PART II : HEATS OF ADSORPTION AND ENERGIES OF ACTIVATION

By

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ABSTRACT

The heats of adsorption and the energies of activation have been calculated, from the data of adsorption of fluorescein on hydrous molybdic oxide. Further, the irreversibility of the adsorption has also been studied. These results establish the fact that adsorption of fluorescein on hydrous molybdic oxide is a typical case of chemisorption, possibly preceded by physical adsorption.

In a previous communication (1), it has been established that the hydrous molybdic oxide precipitated from a solution of ammonium molybdate with HCl is a good adsorbent for the acidic dye, fluorescein. Further, it has been observed that the amount of the dye adsorbed increases both with time and temperature. The results show that the adsorption of fluorescein on hydrous molybdic oxide is mainly a phenomenon of chemisorption, possibly preceded by physical adsorption. The present paper records the values of the heats of adsorption and energies of activation, which confirm the inferences regarding the nature of adsorption of fluorescein on hydrous molybdic oxide.

EXPERIMENTAL

The experimental details of preparing a fine suspension of the hydrous molybdic oxide and the study of adsorption of fluorescein are as described in a preceding paper (1). The results obtained at different temperatures are graphically represented in Fig. 1.

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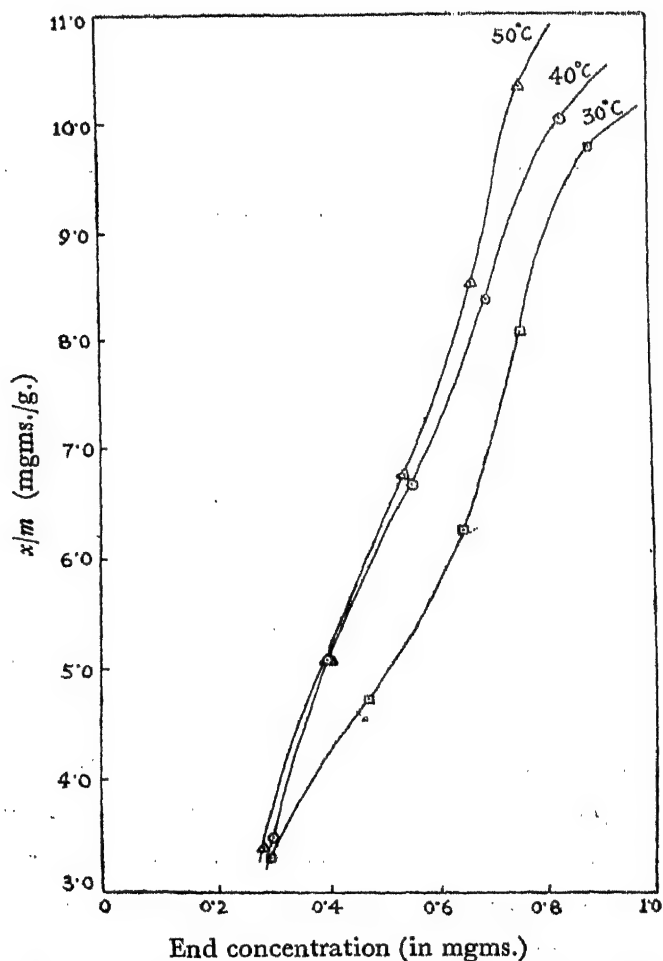
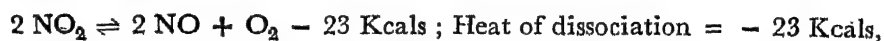


Fig. 1. Adsorption isotherms (time of contact : 3 hrs.)

DISCUSSION

The adsorption isotherms are S shaped, being convex to the concentration axis. This has been explained (1) as due to the nature of the dye anions in solution, where they exist in a highly associated state, *i.e.*, ionic micellar state. So, the adsorption of fluorescein is associated with the dissociation of the aggregate micelles.

Since the adsorption of fluorescein involves the dissociation of micelles into simpler ones, the total heat of adsorption observed should also include the heat of dissociation of the aggregated anions. As several dissociation processes are highly endothermal, *e.g.*,



it may be presumed that the heat of adsorption in the present case may show a

negative value. To verify this, the isosteric heats of adsorption have been calculated according to the relation suggested by Ghosh and Hajela (2)

$$\frac{RT_1 - T_2}{T_1 - T_2} \cdot \ln \frac{C_1}{C_2} = Q(\text{isosteric})$$

where C_1 and C_2 are the end concentrations for the same amount of the dye adsorbed at temperatures T_1 and T_2 . The values of C_1 and C_2 have been extrapolated. The results are given in Table 1.

TABLE 1
Heats of adsorption
Amount of the adsorbent = 0.2159 gms of MoO_3 /250 ml.
Time of contact = 3 hours.

Amount adsorbed x/m	End. conc. C_1 at 30°C (T_1)	End. Conc. C_2 at 40°C (T_2)	Q (30°–40°) Cals/mole.
5.0	0.508	0.39	– 4982
6.0	0.630	0.50	– 4352
7.0	0.712	0.59	– 3542
8.0	0.760	0.692	– 1766
9.0	0.810	0.75	– 1451

The negative values of the heats of adsorption confirm the arguments already put forth. The nature of the adsorption isotherms, which are convex to the concentration axis indicates that the heat of adsorption is less than the heat of dissociation of the dye micelles, which also suggests the negative values for the total heats of adsorption.

It is seen from Table 1, that with the increase of dye adsorbed, the heat of adsorption continuously decreases. Craford and Tamkins (3) have reported similar results in the case of adsorption of SO_2 , NH_3 , NO_2 , etc. on BaF_2 crystals. The fall in the heat of adsorption may be attributed to two reasons. The one considered by Taylor and Liang (4) is due to surface heterogeneity. On a heterogeneous surface, the most active sites will be covered first as the adsorption is likely to proceed more rapidly on them and with increasing amount of adsorption, sites of lessening activity will be covered and the heat of adsorption may, therefore, continuously decrease. The other reason may be the increasing repulsive field in the first layer with the increasing coverage and the formation of multimolecular layers on the adsorbent.

Velocity of adsorption and Activation energies

Fig. 2 shows that the adsorption of the dye increases with time. The adsorption of such dye stuffs as Duramol Blue e.g. 300 on Nylar and Crystal Violet on

chromic oxide (5) increases with time. The rate of adsorption which is fairly rapid in the beginning becomes slow with time and the slope of the curve tends to decrease suggesting chemisorption.

It is seen that none of the different equations, *e.g.*, for mono- ; bi- or ter-molecular order reactions govern the kinetics of the adsorption of fluorescein (Table 2).

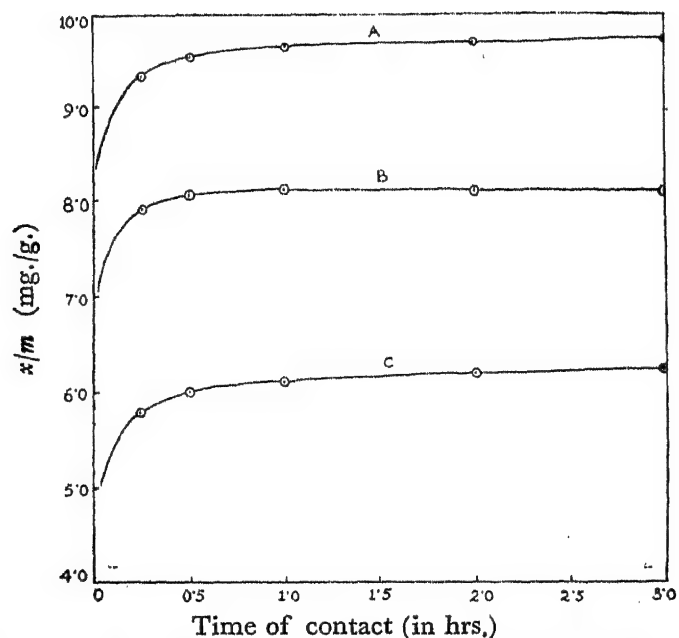


Fig. 2. Effect of time on the adsorption of fluorescein.

Initial amount of the dye : A = 3.0 mgms., B = 2.5 mgms., C = 2.0 mgms.

TABLE 2

Kinetics of adsorption of Fluorescein

Initial amount of the dye = 3 mgms/250·ml.

Amount of the adsorbent = 0.2159 gms. of MoO₃/250 ml.

Temperature = 30°C.

Time (minutes)	I order reaction	II order reaction	III order reaction
15	0.0707	0.0419	0.0271
30	0.0373	0.0224	0.0155
60	0.7189	0.0118	0.0081
120	0.0098	0.0062	0.0056
180	0.0065	0.0041	0.0029

Since the rate of adsorption is affected by temperature it is desirable to calculate the energy of activation so as to throw some more light on the nature of adsorption. Taking into account the Arrhenius theory of reaction rates, Ghosh et al (*loc. cit.*) have derived an equation for calculating the energy of activation as :

$$-\frac{E}{R} \frac{1}{T_1} - \frac{1}{T_2} = \ln \left[\frac{dx}{dt} \right]_{T_1} - \ln \left[\frac{dx}{dt} \right]_{T_2}$$

where E = the energy of activation.

Using the above relation, the values of $\left[\frac{dx}{dt} \right]_{T_1}$ and $\left[\frac{dx}{dt} \right]_{T_2}$ can be calculated from the graph, (fig. 3) between the end concentrations at different

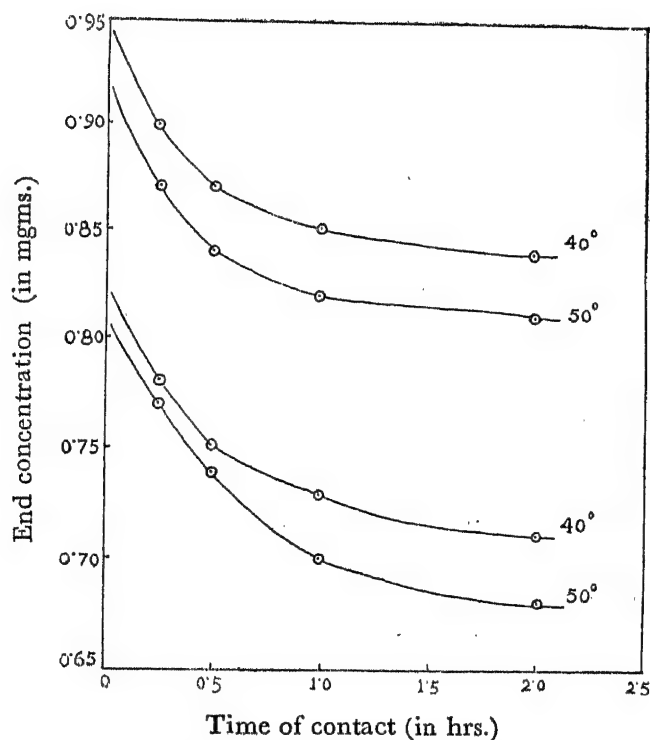


Fig. 3. Plot showing the end concentration against time of contact for calculating the energy of activation.

temperatures by extrapolating the time dt for the same difference of end concentrations at temperatures T_1 and T_2 .

TABLE 3

Energies of activation

Amount of the adsorbent = 0.2159 gms. of MoO_3 /250 ml.

Time of contact = 3 hrs.

End conc. between	$\log \frac{dc}{dt}$	$\log \frac{dc}{dt}$	E cal/mole
(M)	(40°C)	(50°C)	
0.73 - 0.78	2.8539	1.0458	8878
0.725 - 0.775	2.8069	1.0458	11060
0.72 - 0.77	2.7213	1.0458	15020

The energy of activation is positive although its magnitude is not high as compared to that observed for ordinary chemical reactions. There are a number of publications on the kinetics of chemisorption. Recently, Sastri and Srinivasan (6) have, from their studies of adsorption of H_2 on cobalt catalysis, provided ample evidence for the concept of activated adsorption.

Irreversibility of adsorption

The physical adsorption and chemisorption are usually distinguished on the basis of the difference of their reversibility with respect to temperature and concentration. The removal of chemisorbed substance from the surface is usually difficult while the physical adsorption is reversible.

It is clear from Table 4 that the end concentration of the supernatant dye after complete adsorption is double the end concentration, 50% of which is diluted by the same volume of water and kept for desorption for three days. This shows that the adsorption is irreversible as no desorption takes place. Hence it may be inferred that the adsorption of fluorescein is a process of chemisorption and involves the formation of some stable adsorption complex.

TABLE 4

Irreversibility of adsorption

Amount of the adsorbent = 0.2025 of MoO_3 /250 ml.

Temperature = 28°C.

Amount of the dye added (mgms.)	End conc. after 3 days	End. conc. after 50% dilution and desorption for 3 days	
		Theoretical	Observed
3.0	0.80	0.40	0.40
2.5	0.64	0.32	0.32
2.0	0.52	0.26	0.26
1.5	0.36	0.18	0.18

In view of the above observations *i.e.*, the increase in adsorption with temperature, the positive activation energy, the slow rate of adsorption and the irreversibility of adsorption it is concluded that the adsorption of fluorescein on hydrous molybdic oxide is a typical case of chemisorption, possibly preceded by physical adsorption in the earlier stages.

The authors are grateful to Prof. A. K. Bhattacharya, Head, Department of Chemistry, University of Saugar, for his keen interest in these investigations.

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ADSORPTION OF FLUORESCEIN ON HYDROUS MOLYBDIC OXIDE

PART III : COMPARATIVE ADSORPTIVE CAPACITIES AND EFFECT OF ELECTROLYTES ON THE ADSORPTION

By

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ABSTRACT

Three samples of hydrous molybdic oxide were obtained by precipitating from ammonium molybdate solution with (a) 10% deficient, (b) equivalent and (c) 10% excess of HCl. The adsorption studies of fluorescein on these samples reveal that the adsorptive capacities lie in the order $C > B > A$. The results have been explained from the point of view of amphoteric nature of the oxide and a mechanism has been suggested to explain such a behaviour. It has been found out that Freundlich and Langmuir's adsorption equations are not applicable. Further, the data show that the effect of electrolytes in decreasing the amount of fluorescein adsorbed lies in the order of $\text{Na}_2\text{SO}_4 > \text{NaCl}$.

In a previous communication¹ it has been shown that hydrous molybdic oxide is a good adsorbent for the acidic dye, fluorescein and that the adsorption is mainly a process of chemisorption, possibly preceded by physical adsorption. In the present paper, we have studied the adsorbability of different samples of molybdic oxide, the applicability of Freundlich and Langmuir's equations and the effect of electrolytes on the adsorption of fluorescein.

EXPERIMENTAL

Three samples of hydrous molybdic oxide were precipitated as follows :—

Sample	Vol. of (NH_4) ₆ MoO ₇ O ₂₄ (0.1 M.)	Vol. of HCl. (2.5 M.)	Temperature=27°C.
			Remarks (Amount of acid for precipitation)
A	100 ml.	21.6 ml.	10% deficient
B	100 ml.	24.0 ml.	Equivalent
C	100 ml.	26.4 ml.	10% Excess

The experimental details regarding the preparation of a fine suspension of the oxide and the study of the adsorption of the dye were as described.¹ The results obtained at 30°C are recorded in table 1.

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TABLE 1

Verification of Freundlich and Langmuir's adsorption equations

Time of contact=3 hrs.

Temperature = 30°C.

Sample	Initial concentration of dye (mgms/250 ml.)	End Concentration. (mgms/250 ml.)	Amount adsorbed. (x/m)	$\log c$	$\log x/m$	$\frac{c}{x/m}$
A	3.0	0.92	9.636	1.9638	0.9839	0.0955
	2.5	0.78	7.968	1.8921	0.9012	0.0979
	2.0	0.68	6.115	1.8325	0.7864	0.1112
	1.5	0.50	4.633	1.6990	0.6659	0.1080
	1.0	0.31	3.196	1.4914	0.5046	0.0970
B	3.0	0.90	9.774	1.9494	0.9901	0.0911
	2.5	0.76	8.060	1.8808	0.9063	0.0943
	2.0	0.66	6.263	1.8129	0.7961	0.1040
	1.5	0.47	4.771	1.6721	0.6786	0.0985
	1.0	0.29	3.290	1.4624	0.5172	0.0881
C	3.0	0.89	10.470	1.9494	1.0119	0.0850
	2.5	0.70	8.936	1.8808	0.9363	0.0879
	2.0	0.65	6.701	1.8129	0.8262	0.0969
	1.5	0.46	5.162	1.6628	0.7128	0.0891
	1.0	0.28	3.574	1.4472	0.5532	0.0783

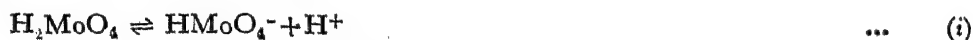
The results show that the adsorptive capacity of the samples for the acidic dye, fluorescein, lies in the order $C > B > A$. These observations are explainable from the amphoteric character of molybdic oxide.

Gapan² has suggested that, theoretically, the adsorption of anions should increase with the decrease in pH. Ghosh and Dey³ have reported that the basic or the acidic character of amphoteric oxides can be suitably evoked by controlling the pH of the medium from which they are precipitated and have advanced a hypothesis to explain the amphoteric behaviour of insoluble hydrous oxides as :



Equation (i) shows the basic character of the oxide while Equation (ii) the liberation of a proton explaining its acidic character. Equation (iii) points out that the oxide becomes comparatively inactive due to the mutual neutralisation of its acidic and basic properties. They have definitely established that factors like ageing or heating the hydrous oxide promotes the formation of the inert variety.

A similar mechanism is suggested here to account for the reactions on the surface of the molybdic acid :



Equation (i) shows the acidic character of the oxide facilitating the adsorption of cations. Equation (ii) illustrates the basic character of the oxide, favouring the adsorption of anions. Equation (iii) explains how the oxide becomes comparatively inert due to the mutual neutralisation of its acidic and basic properties. There is evidence for the existence of MoO_2OH radical. Wardlaw and James⁴ prepared pyridinium molybdenyl dichloride and showed that MoO_2OH exists as an intermediate radical. According to the equation (ii) if the acidity of the system is increased, the forward reaction is favoured and the basic character of the oxide becomes more pronounced with greater adsorption of anions.

The samples, A, B and C, differ in the increasing acidity of the medium from which they are precipitated, thus enhancing respectively their basic character and this results in an increasing order of the adsorption of fluorescein.

The plots between $\log x/m$ and $\log c$ (Table 1, fig. 1) and between $(c/x)/m$ and c (Table 1, fig 2) do not show linearity indicating that the equations of Freundlich and Langmuir respectively do not apply here. This is probably due to the limiting applicability of these equations⁵.

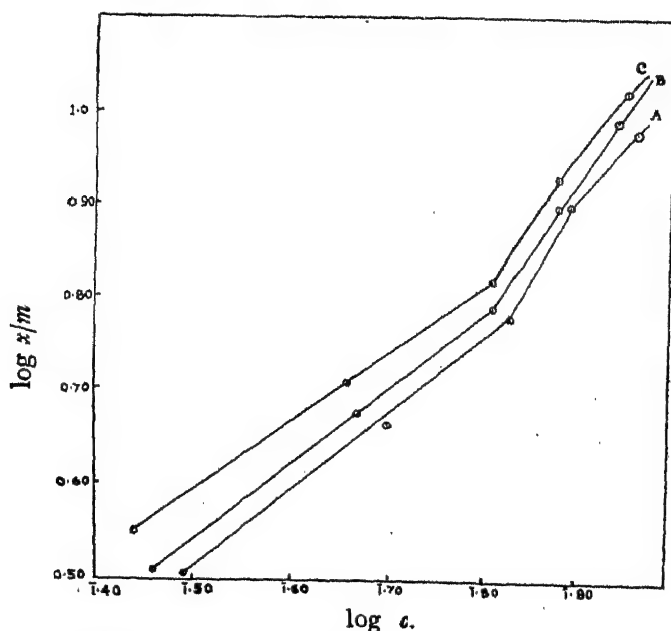


Fig. 1. Verification of Freundlich Adsorption Equation at 30°C.

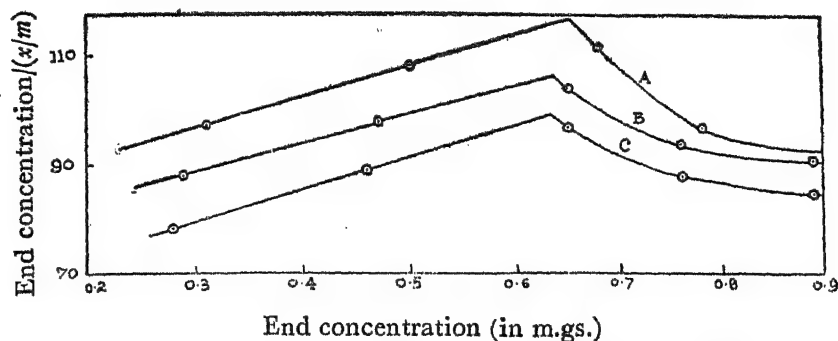


Fig. 2. Verification of Langmuir's Equation at 30°C.

Effect of Electrolytes on the Adsorption :—

The addition of acids, bases and salts to solutions of acidic and basic dyes influence their adsorption according to the rules formulated by Bancroft⁶ and Pelet-Jolivet⁷ for simultaneous adsorption from mixtures of electrolytes. They opine that acid dyes are taken up most strongly in acid solutions and least in basic solutions and highly adsorbed anions decrease the amount of the acid dye taken up. Further, an increase in the strength of the electrolyte added causes a decrease in the extent of adsorption of acid dyes.

Tables 2 and 3 give the results of adsorption of fluorescein on molybdic oxide in presence of Na_2SO_4 and NaCl respectively.

TABLE 2
Effect of Na_2SO_4 on adsorption.

Time of contact : 3 hrs.

Temperature = 30°C.

Sample	Amount of dye added (mgms/250 ml.)	x/m in presence of Na_2SO_4 of conc.				
		0.0 M (blank)	0.005 M	0.01 M	0.025 M	0.05 M
A	3.0	9.777	9.679	9.579	9.252	8.986
	2.0	6.518	6.469	6.320	6.122	5.926
B	3.0	9.924	9.924	9.574	9.282	9.084
	2.0	6.518	6.469	6.320	6.222	5.928
C	3.0	9.974	9.779	9.679	9.333	9.084
	2.0	6.616	6.518	6.418	6.270	5.966

TABLE 3

Effect of NaCl on adsorption.

Time of contact : 3 hrs.

Temperature = 30°C.

Sample	Amount of dye added (mgms/250 ml.)	x/m in presence of NaCl of conc.			
		0.0 M (blank)	0.01 M	0.025 M	0.05 M
A	3.0	9.777	9.777	9.679	9.579
	2.0	6.518	6.518	6.469	6.418
B	3.0	9.924	9.777	9.777	9.679
	2.0	6.518	6.518	6.485	6.469
C	3.0	9.974	9.777	9.777	9.679
	2.0	6.616	6.518	6.518	6.518

The results show that the effect of electrolyte in decreasing the amount of the dye adsorbed is in the order, $\text{Na}_2\text{SO}_4 > \text{NaCl}$.

It has been established⁹ that the sulphate ion is adsorbed to a greater extent than the chloride ion on molybdic oxide. Thus in accordance with the rules of Bancroft and Pelet-Jolivet mentioned earlier, the bivalent sulphate ion decreases the adsorption of fluorescein more than the less strongly adsorbed chloride ion. Further, it will be noted that the adsorption of fluorescein decreases with an increase in the concentration of the added electrolyte.

The authors are grateful to Prof. A. K. Bhattacharya, Head, Department of Chemistry, for his keen interest in these investigations.

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EQUILIBRIA STUDIES OF HYDROUS MOLYBDIC OXIDE IN DILUTE ACID AND ALKALI

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ABSTRACT

The solubility of hydrous molybdic oxide has been studied in water, dilute HNO_3 and dilute NaOH solutions at 26°C . The data reveal that the solubility increases with increasing quantities of both acid and alkali, and with time. The latter has been ascribed to the transformation of β - form of the monohydrate of MoO_3 to the more soluble α - form with ageing. The high solubility of molybdic acid in alkaline solutions and low in acid solutions indicate that molybdic acid is relatively a strong acid.

The existence of a definite monohydrate of molybdic oxide, $\text{MoO}_3 \cdot \text{H}_2\text{O}$, has been established both by x-ray¹ and tensio-eudiometric methods.² The monohydrate exists in two allotropic modifications α and β . The α - form differs from the β - form in having a more definite crystal character. The solubility of this monohydrate is considerably low. Rosenheim and Davidson³ determined the solubility of molybdic acid and reported a value of 0.2619 gm of MoO_3 per 100 gms of water at 24.6°C . Debray⁴ found that 100 parts of cold water dissolve 0.18 part of MoO_3 whereas Hatchell⁵ said that 100 parts of hot water dissolve only 0.104 part of the trioxide.

In view of the above controversial observations, it was thought worthwhile to redetermine the solubility of molybdic acid and the present communication deals with this property of molybdic acid in water, dilute HNO_3 and NaOH solutions as also the effect of temperature and age on the same. Further, the solubility data could be used to secure further information as to the character of ions of molybdic acid in dilute solutions of acid and alkali.

EXPERIMENTAL

A sample of the suspension of the hydrous molybdic oxide was prepared and constituents estimated as described in a preceding paper⁶. Standard solutions of HNO_3 (C. P.) and NaOH (AnalaR, BDH) were prepared and their strengths determined by titrations.

10 ml of the suspension of molybdic acid were introduced into each of various 100 ml flasks. Increasing quantities of either dilute HNO_3 or NaOH were added to the suspensions and the total volumes were raised to 100 ml. These solutions were shaken thoroughly and left overnight at the room temperature for the attainment of saturation and equilibrium. A definite volume of the solution was then centrifuged and the pH measured with a Beckman pH meter and the molybdenum content was determined both gravimetrically as lead molybdate and volumetrically.⁷ The results obtained by the methods agreed within $\pm 0.5\%$.

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In order to determine the solubilities at 40° and 50°C, the suspensions with the added acid or alkali were maintained at the respective temperatures in a thermostat for two hours. After cooling, the solutions were made upto 100 ml and the Mo content was determined. To study the effect of ageing, the suspensions with the added acid or alkali were made upto the mark in 100 ml flasks and allowed to age for a period of 25 days at the room temperature. The Mo content in these samples was also determined as before. The results are recorded in table 1.

TABLE I

Effect of temperature and age on the solubility of Molybdic oxide

Solvent	Volume (ml) of HNO ₃ (1.079 N) or NaOH (0.098 N) added	Solubility C. gms of MoO ₃ /100 ml.			
		26°C	40°C	50°C	when aged for 25 days
Water	—	0.01559	0.02069	0.02638	0.02158
HNO ₃	5.0	0.01679	0.01879	0.01979	0.01859
	7.5	0.01779	0.02088	0.02459	0.01919
	10.0	0.02098	0.02398	0.02758	0.02398
	12.5	0.02338	0.02738	0.03118	0.02878
	15.0	0.02578	0.02878	0.03238	0.02888
	17.5	0.03018	0.33180	0.03597	0.03158
NaOH	0.5	0.02758	0.03018	0.03238	0.03197
	1.0	0.03537	0.03854	0.04198	0.03937
	1.5	0.04615	0.04732	0.05396	0.04717
	2.0	0.04719	0.52050	0.05755	0.04737
	2.5	0.05115	0.06010	0.06835	0.05217
	3.0	0.06356	0.06738	0.07155	0.06536

DISCUSSION

The results show that the solubility of molybdic acid in water is rather low (0.01599 gms. of MoO₃ in 100 ml of water at 26°C.). This value is different from those obtained by others. Mehrotra and Ghosh⁹ have shown that the solubility of hydrous oxides depends upon the conditions of precipitation, the temperature of dissolution and age of the sample. This may be the reason for the variation in the values mentioned above.

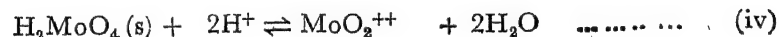
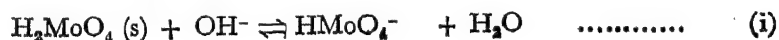
It is widely accepted that ageing diminishes the chemical reactivity as also the solubility of hydrous oxides. But the results recorded in table 1 show that there is an increase in solubility with age. It has already been pointed out that the monohydrate of MoO_3 exists in two allotropic modifications. Further, Weiser⁹ is of the opinion that the gradual changes in properties with ageing are attributed to a transformation of one allotropic modification to another. A comparative study of these two, α - and β - forms will provide an explanation for the increased solubility with age.

Earlier workers such as Vivier¹⁰ and Rosenheim and Davidson designate the monohydrate of MoO_3 precipitated by acidification of normal molybdates as the β - form to distinguish it from the α - form which is formed in asbestos-like white needles when a solution of the dihydrate is kept at $40^\circ - 60^\circ\text{C}$. The α - form readily settles down from a suspension in water and is more soluble than the β - form. In the course of the present investigations, it was observed that a fresh sample of molybdic oxide takes considerable time to settle down from an agitated suspension in water whereas the aged sample readily does so. It may, therefore, be suggested that the fresh sample is the β - modification which changes on to the α - form with ageing. This explains the anomaly, i.e., the increasing solubility with age.

It is well known that by virtue of its amphoteric nature, molybdic acid dissolves both in acids and alkalis. This may be explained as follows (i) the solubility of molybdic acid in NaOH is due to the extent to which the weak acid, H_2MoO_4 , is neutralised by the strong base and (ii) that in the presence of HNO_3 is mainly due to the neutralisation of the weak base, $\text{MoO}_2(\text{OH})_2$ by the strong acid.

In several recent publications¹¹, the amphoteric nature of Ni , Co , Hg , U , Sb , As oxides has been explained from solubility studies. The studies of equilibria of antimony oxide in NaOH and HCl solutions indicate that antimony is present in both the cases as a monovalent ion. The solubility data of As_2O_3 in NaOH reveal that monobasic, mono-, di- and triarsenate ions are formed in alkaline solution. It appears, therefore, that the solubility data of molybdic oxide in dilute HNO_3 and NaOH could be well used in examining the nature of the ions of molybdic acid in acid and alkaline solutions.

Garrett et al¹¹ suggested probable reactions to account for the solubilities of many amphoteric oxides in dilute acids and alkalis. On similar grounds, the possible equilibria of molybdic acid, H_2MoO_4 , in acid and alkali may be represented by the following equations :—



Equilibria in base and acid solutions :—

The method of Garrett and Gayer¹² has been adopted here for evaluating the equilibrium constants using the data in table 2, the equilibrium constants K_1 and K_2 were calculated as :

$$K_1 = \frac{m \text{HMoO}_4^- \cdot \gamma \text{HMoO}_4^-}{m \text{OH}^- \cdot \gamma \text{OH}^-}$$

$$K_2 = \frac{m \text{MoO}_4^{--} \cdot \gamma \text{MoO}_4^{--}}{m (\text{OH}^-)^2 \cdot \gamma (\text{OH}^-)^2}$$

The ratio $\frac{\gamma \text{HMoO}_4^-}{\gamma \text{OH}^-}$ may be assumed to be unity over the concentration range studied. The value of $m \text{HMoO}_4^-$ or $m \text{MoO}_4^{--} =$ total molybdic acid—undissociated molybdic acid. Since molybdic acid is a weak acid, the undissociated acid can be determined by extrapolating the solubility curve for molybdic acid in base to $m \text{OH}^- = 0$. This value was found out to be $= 88 \times 10^{-3}$.

TABLE 2

Solubility of molybdic acid in dilute NaOH solutions at 26°C

Initial moles of NaOH/100 ml.	Gm. moles of MoO ₃ /100 ml.	pH of the solution after saturation	$K_1 = \frac{\text{MoO}_3}{\text{OH}^-}$	$K_2 = \frac{\text{MoO}_3}{(\text{OH}^-)^2}$
2.475×10^{-6}	9.350×10^{-3}	3.50	1.802×10^{-2}	5.020×10^7
4.950×10^{-6}	9.895×10^{-3}	4.00	1.758×10^{-2}	4.479×10^7
9.900×10^{-6}	11.090×10^{-3}	4.10	1.838×10^{-2}	2.336×10^7
4.950×10^{-5}	16.490×10^{-3}	4.25	1.553×10^{-2}	3.138×10^6
1.485×10^{-4}	29.680×10^{-3}	4.75	1.460×10^{-2}	9.466×10^5

TABLE 3

Solubility of molybdic acid in dilute HNO₃ solutions at 26°C

Initial moles of HNO ₃ /100 ml.	Gm. moles of MoO ₃ /100 ml.	pH of the solution after saturation	$K_3 = \frac{\text{MoO}_3}{\text{H}^+}$	$K_4 = \frac{\text{MoO}_3}{(\text{H}^+)^2}$
2.423×10^{-2}	1.949×10^{-2}	0.95	4.867×10^{-1}	2.008×10^{-1}
1.414×10^{-2}	1.469×10^{-2}	1.25	4.943×10^{-1}	3.497×10^{-1}
1.009×10^{-2}	1.259×10^{-2}	1.40	4.849×10^{-1}	4.807×10^{-1}
8.076×10^{-3}	1.140×10^{-2}	1.45	4.581×10^{-1}	5.627×10^{-1}
4.038×10^{-3}	9.859×10^{-3}	1.65	5.423×10^{-1}	1.343×10^{-2}
2.019×10^{-3}	8.496×10^{-3}	1.95	4.904×10^{-1}	2.429×10^{-2}

The results (Table 2) show that whereas the K_1 values are almost constant, those of K_2 are not so. Since it is well known that several types of molybdate ions exist depending upon the pH of the solution, it cannot be assumed that the same type of molybdate ion is formed by the addition of varying quantities of NaOH. Hence, K_2 values do not show a constancy. The constancy in K_1 values, on the other hand, shows that the reaction indicated by equation (i) is primarily responsible for the solubility of molybdic acid and HMoO_4^- ions are probably the intermediate ones to form subsequently the various molybdate ions depending upon the pH of the solution. The work of Rosenheim and Felix¹³ and Ghosh and Biswas¹⁴ support the above view. They have established that acid salts of the type, $\text{RH}(\text{O}(\text{MoO}_3)_4)$ do exist as intermediate ones which change later to the type $\text{R}_2(\text{O}(\text{MoO}_3)_4)$ depending upon the pH of the solutions.

The solubility of molybdic acid in dilute nitric acid can be accounted for by the equations, (iii) and (iv). The equilibrium constants K_3 and K_4 were calculated from the data in table 3.

$$K_3 = \frac{m \text{MoO}_2\text{OH}^+ \cdot \gamma \text{MoO}_2\text{OH}^+}{m \text{H}^+ \cdot \gamma \text{H}^+}$$

$$K_4 = \frac{m \text{MoO}_2^{++} \cdot \gamma \text{MoO}_2^{++}}{m (\text{H}^+)^2 \cdot \gamma (\text{H}^+)^2}$$

The ratio $\frac{\gamma \text{MoO}_2\text{OH}^+}{\gamma \text{H}^+}$ can be assumed to be unity over the concentration range studied. The value of $m\text{MoO}_2\text{OH}^+$ or $m\text{MoO}_2^{++}$ was obtained from the relationship, $m\text{MoO}_2\text{OH}^+$ or $m\text{MoO}_2^{++} = \text{total molybdic acid} - \text{undissociated acid}$ and that of the undissociated acid was found out to be 7.7×10^{-3} from an extrapolation of the solubility in acid solutions to $m\text{H}^+ = 0$.

It will be noted here, too, that K_4 values do not show any constancy whereas K_3 values do so fairly. This indicates that the solubility of molybdic acid in dilute mineral acid is explainable mainly by the equation (i) which shows the formation of MoO_2OH^+ . It should be remembered, here, that Wardlaw¹⁵ has shown the existence of this ion, MoO_2OH^+ , as an intermediate one.

The authors are grateful to Prof. A. K. Bhattacharya, Head, Department of Chemistry, for his keen interest in these investigations.

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DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS BY HYDROUS OXIDES

PART III. HYDROUS Fe (III) OXIDE

By

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ABSTRACT

The paper describes the decomposition of hydrogen peroxide catalysed by three samples of hydrous ferric oxide, prepared at room temperature, by adding (a) 5% excess, (b) equivalent and (c) 5% deficient amounts of caustic soda solution, to a ferric chloride solution. The results indicate that the rate of decomposition follows unimolecular law with stronger solutions of the peroxide, but the order tends to increase with decreasing concentrations of hydrogen peroxide, specially at higher temperatures and with very dilute peroxide, solutions. The catalytic activity of the three samples is in the order : A, B, C.

It is well known that hydrous ferric oxide catalyses decomposition of hydrogen peroxide. Here a detailed study of the decomposition has been made in the presence of the hydrous oxide prepared by adding different amounts of alkali to ferric chloride solution.

EXPERIMENTAL

The three samples of the hydrous ferric oxide were precipitated from 200 ml of ferric chloride solution containing 42.11 gm of FeCl_3 per litre, by adding calculated volumes of 2.5 N caustic soda solutions at room temperature. As it was found that on prolonged washing the hydrous oxide precipitate tends to peptise, 25 ml of 0.5N potassium sulphate was added during the precipitation.

These samples of hydrous ferric oxide were washed and estimated for their iron content volumetrically. The hydrous oxide suspensions were diluted with calculated volumes of distilled water so that 5 ml of the suspensions of each contained the same amount of iron. The pH of the samples A, B and C were 3.8, 3.5, and 3.5, respectively.

A conical flask containing 75 ml of hydrogen peroxide solution of known concentration and the bottle containing hydrous oxide suspension were kept in a thermostat to attain the desired temperature. 5 ml of the suspension were drawn after shaking the bottle well and were added to the flask. At different intervals, the flask was well shaken and 5 ml of the reaction mixture were drawn out. The reaction was checked with 10-15 ml of 4N sulphuric acid solution and the solution was estimated for undecomposed hydrogen peroxide against a standard potassium permanganate solution of strength equal to that of the peroxide in the conical flask at the time of starting the reaction.

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Temperature 30°C

Conc. of H_2O_2 soln = 0.05N

TABLE 1

Sample A		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	3.33	0.0111
30	2.41	0.0105
45	1.75	0.0101
60	1.14	0.0107
75	0.88	0.0100
90	0.61	0.0101
105	0.44	0.0100
120	0.30	0.0101

TABLE 2

Sample B		
Time (min)	KMnO ₄ used (ml)	First order constants $(K/2.303)$
0	5.00	—
15	4.04	0.0061
30	3.25	0.0062
45	2.59	0.0063
60	2.10	0.0062
75	1.75	0.0060
90	1.40	0.0061
105	1.14	0.0061
120	0.88	0.0062

Conc. of H_2O_2 soln. = 0.05N

TABLE 3

Sample C		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	4.12	0.0056
30	3.46	0.0053
45	2.80	0.0056
60	2.37	0.0054
75	1.93	0.0055
90	1.58	0.0055
105	1.32	0.0055
120	1.14	0.0053

Conc. of H_2O_2 soln. = 0.005N

TABLE 4

Sample A		
Time min.	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	3.42	0.0110
30	2.46	0.0102
45	1.75	0.0101
60	1.40	0.0092
75	1.05	0.0090
90	0.88	0.0083
105	0.79	0.0076
120	0.61	0.0076

Conc. of H_2O_2 soln. 0.005N

TABLE 5

Sample B		
Time (min)	KMnO used (ml)	First order constants $K/2.303$
0	5.00	—
15	4.04	0.0061
30	3.25	0.0062
45	2.54	0.0065
60	2.10	0.0062
75	1.75	0.0060
90	1.49	0.0058
105	1.32	0.0055
120	1.14	0.0053

Conc. of H_2O_2 soln. 0.005N

TABLE 6

Sample C		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	4.04	0.0061
30	3.16	0.0066
45	2.63	0.0062
60	2.20	0.0059
75	1.84	0.0057
90	1.58	0.0055
105	1.32	0.0055
120	1.14	0.0053

Temperature 35°C
Conc. of H_2O_2 soln—0.05N

TABLE 7

Sample A		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	2.50	0.0201
30	1.60	0.0164
45	1.00	0.0155
60	0.65	0.0147
75	0.40	0.0146
90	0.25	0.0144
105	0.20	0.0133
120	0.15	0.0127

TABLE 8

Sample B		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	3.70	0.0087
30	2.70	0.0089
45	2.15	0.0081
60	1.60	0.0082
75	1.20	0.0082
90	9.00	0.0082
105	0.70	0.0081
120	0.60	0.0076

Temperature 35°C

TABLE 9

Sample C		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	3.90	0.0072
30	3.10	0.0069
45	2.40	0.0070
60	1.90	0.0070
75	1.50	0.0069
90	1.15	0.0070
105	0.90	0.0070
120	0.70	0.0071

Temperature 40°C

TABLE 10

Sample A		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	2.95	0.0151
30	1.76	0.0151
45	0.91	0.0164
60	0.57	0.0157
75	0.34	0.0155
90	0.23	0.0148
105	0.11	0.0157

Temperature 40°C

TABLE 11

Sample B		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	3.52	0.0101
30	2.61	0.0094
45	1.70	0.0104
60	1.25	0.0100
75	0.80	0.0106
90	0.57	0.0104
105	0.45	0.0099
120	0.34	0.0097

TABLE 12

Sample		
Time (min)	KMnO ₄ used (ml)	First order constants $K/2.303$
0	5.00	—
15	3.52	0.0101
30	2.61	0.0094
45	1.93	0.0091
60	1.25	0.0101
75	0.91	0.0098
90	0.68	0.0096
105	0.45	0.0099
120	0.34	0.0097

The results of the preceding tables show that the decomposition of hydrogen peroxide in presence of hydrous ferric oxide samples is of first order with stronger solutions of the peroxide. The order, however, tends to increase with very dilute solutions of the peroxide specially with the suspension of sample A. At higher temperatures the catalytic activity of the samples B and C tends to be the same, which otherwise lies in the order : $A > B > C$.

The temperature coefficient, energy of activation E , frequency factor A and entropy of activation ΔS have been calculated for the samples B and C from the tables 2, 8, 11, and 3, 9 and 12.

TABLE 13

Temperature range	Temperature coefficient		E in cal.	
	B	C	B	C
30° — 35°C	1.333	1.288	10,608	9,412
25° — 40°C	1.217	1.374	7,234	12,184
30° — 40°C	1.625	1.771	8,948	10,775

TABLE 14

Temp.	Encounters per minute		ΔS in e.u.	
	B	C	B	C
	$A \times 10^{-4}$	$A \times 10^{-4}$		
30°C	1.721	3.316	-47.71	-41.40
35°C	1.795	3.196	-47.20	-41.44
40°C	1.722	3.313	-47.25	-41.44

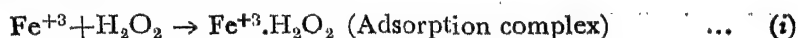
As is usually the case with the heterogeneously catalysed reactions, the energy of activation calculated here is comparatively small.

DISCUSSION

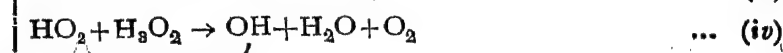
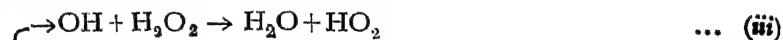
The decomposition of hydrogen peroxide catalysed by Fe^{+3} or Fe^{+2} ion has been investigated by several workers. Various mechanisms have been put forward to account for this catalytic activity. The intermediate formation of a ferrate anion $(FeO_4)^{-}$ was suggested by Bohnsen and Robertson¹ but Manchot and Lehmann² suggested the formation of higher oxide Fe_2O_5 , whilst Bray and Gorin³ are of the opinion that Fe^{+2} is formed. Barb, Baxendale and others⁴ have investigated the decomposition of the peroxide by Fe^{+3} and they suggest that first step is the reduction of Fe^{+3} to Fe^{+2} by HO_2^- a probable anion arising out of the acidic nature of hydrogen peroxide :



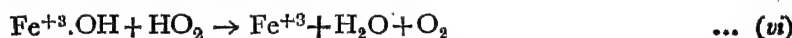
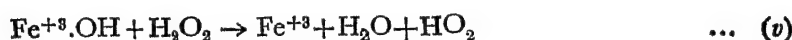
Our results indicate that the hydrous oxide of iron obtained in slightly alkaline medium proves to be the best catalyst in the decomposition of hydrogen peroxide. Ghosh and coworkers from their study of different hydrous oxides have shown their greater adsorptive capacity for cations than anions. The reduction of Fe^{+3} to Fe^{+2} state, which is attended by the action of anion HO_2^- should be least for the hydrous oxide obtained by precipitating with excess of alkali. We are, therefore, of the opinion, that the catalytic activity is due to the intermediate formation of highervalent iron in the presence of hydrogen peroxide. Hence we suggest the following mechanism :



The OH thus liberated may initiate the cyclic decomposition of hydrogen peroxide as suggested by Haber and Willstätter,



and the highervalent iron may also further react with hydrogen peroxide to form back Fe^{+3}



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ELECTROMETRIC STUDIES ON BENTONITES FROM RAJASTHAN

By

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ABSTRACT

The bentonite samples from Rajasthan were converted into H-bentonites by acid leaching. They were titrated potentiometrically in the aqueous and non-aqueous media. Observations in non-aqueous media increase the no. of inflexions and may provide some evidence for additional clay minerals in 'Akli' and 'Gadhi-ka-Giram' bentonites which could not be located from the titration curves in aqueous medium.

The b.e.c., pH and pK values for the two bentonites at the inflexion points have been determined. The results have been discussed in terms of the mineralogical composition of the bentonites.

Conductometric titrations confirmed most of the conclusions arrived at on the basis of potentiometry. The results obtained give a satisfactory explanation of the difference in the general properties of the two bentonites.

Thanks are due to the Director, Mining and Geology, Government of Rajasthan for arranging the supply of bentonite samples.

Electrometric methods have found extensive use in studying the physicochemical properties of soils. Many authors, including Mukherjee^{1,2,3}, Mitra⁴, Marshall⁵, Brindley⁶, Grim⁷, Harmon⁸, Adhikari⁹ and Chakravarti¹⁰ have recommended the use of potentiometric titrations in characterising clay minerals. For example, it has been observed that a H-clay which behaved as a weak monobasic acid with caustic alkalies is largely composed of the mineral montmorillonite while the one with a weak dibasic character is predominantly kaolinitic. On the other hand the tribasic nature of the titration curves indicates the presence of the clay mineral illite.^{11,12} Besides, conductometric methods,¹³ although of limited applicability, have found use in carrying out comparative study on soils and in determining their b.e.c.

Potentiometric titrations in such cases, however, suffer from one major defect, namely, the non availability of all possible inflexion points due to close proximity in the pK values of the different acids constituting the hydrogen clay and the levelling effect of the aqueous media. To overcome this, titrations in the non-aqueous media can be recommended for obtaining more useful information about the acids present in the H-clay. Ruehle¹⁴, Fritz¹⁵, Palit & others¹⁶ have used such methods successfully for the titration of mixtures of weak acids.

The present communication deals with the potentiometric studies in the aqueous and non-aqueous media on two bentonite samples from Rajasthan. The work also includes conductometric studies to confirm and substantiate the results of potentiometry.

The two samples of bentonite were obtained as gift from the Director of Mining and Geology, Udaipur (Rajasthan). Sample No. 1 collected from Akli

was in the form of small flat laminated pieces, greyish brown in colour with a slight reddish hue while sample No. 2 from Gadhi-ka-Giram was greenish white in colour with a soapy touch. Both the bentonites exhibited swelling propertise, the Akli sample showing enormous swelling tendency when brought in contact with water. It could also be easily transformed into a stable suspension by just shaking with distilled water while only a small fraction of the other bentonite passed into a stable suspension.

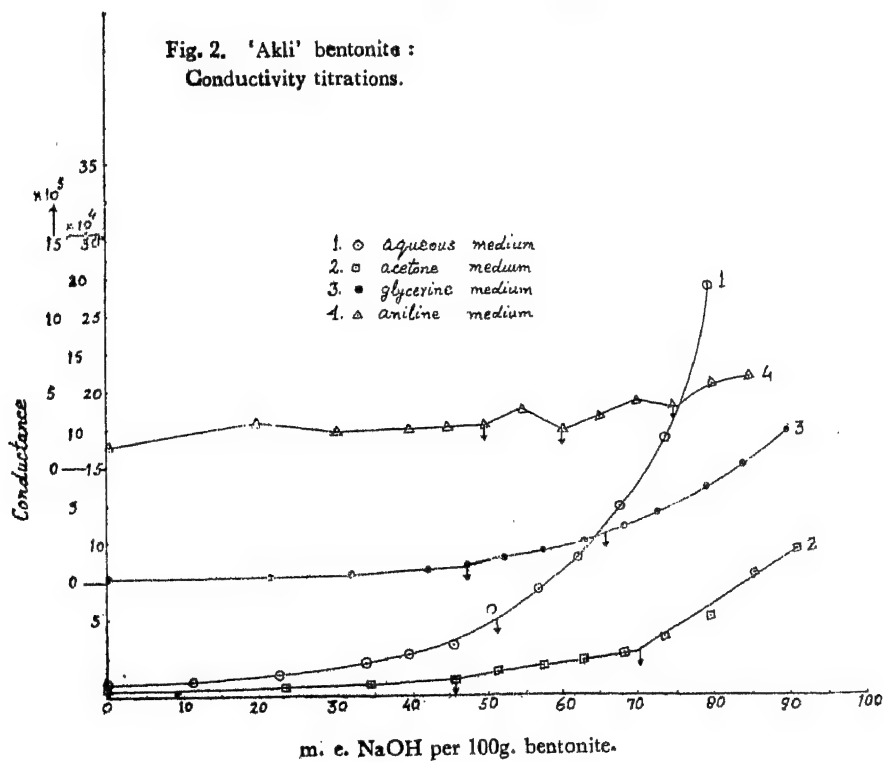
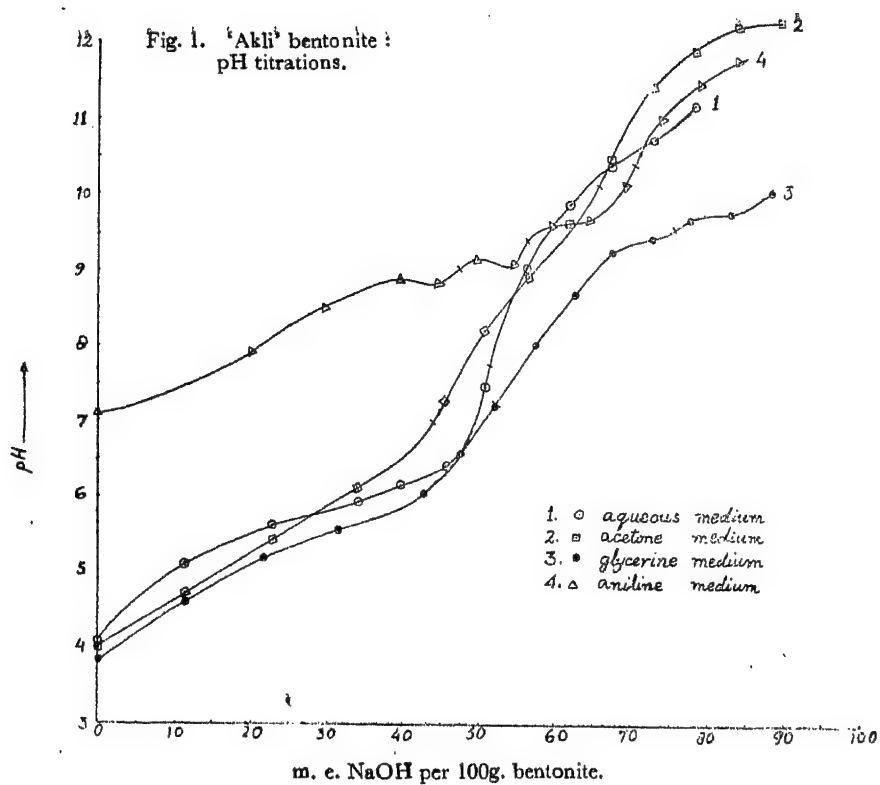
EXPERIMENTAL

Samples of acid bentonites were prepared from 'Akli' bentonite and 'Gadhi-ka-Giram' bentonite by prolonged and careful acid leaching to ensure as full base exchange as possible. The acid clay was then washed free from chlorides and used quickly for the under mentioned titrations.

For carrying out the experiments one gram samples of the freshly prepared acid bentonites were taken in 'pyrex' glass tubes and then treated with varying amounts of 0.1 N NaOH (prepared in aqueous or benzene-methanol (1:4) media), the total volume in each case was made up to 20 cc. either with double distilled water or the organic solvents when carrying out the titrations in non-aqueous media. The mixtures were kept in closed tubes for 48 hours with occasional shaking. A 'Hitachi' pH meter model EPH-2 with saturated calomel and glass electrodes assembly was used throughout for pH measurements. Conductivity measurements were carried out under exactly similar conditions with the help of 'W. T. W.' conductivity bridge and dip type cell. All measurements were done at $30 \pm 1^\circ\text{C}$.

DISCUSSION

The difference in the nature and the composition of the two clay samples under investigation is fairly borne out from the potentiometric studies. Generally speaking well defined inflexions in the pH curves can only be realised when the pK values of a polybasic acid or of the different acids constituting the mixture differ by at least 4 units. That such an ideal behaviour could not be realised in the present investigations is not surprising because of the narrow difference in the pK values of the various acids constituting the two clays. However, on carrying out the titrations in the non-aqueous media, the inflexion points not only become sharper but some new points make their appearance which normally remain masked in a purely aqueous medium. Another interesting behaviour observed in these titrations is that in all cases the inflexions are preceded by an increase in pH except when aniline medium is employed. Here rapid fluctuations in pH were experienced during the course of the measurements and the decrease in pH before emergence of the inflexion in the titration curves may be attributed to the hydrolytic tendency of the salts formed by the interaction of aniline with the acid part of the clays. (Figs 1 and 3, curves 4 and 3 respectively).



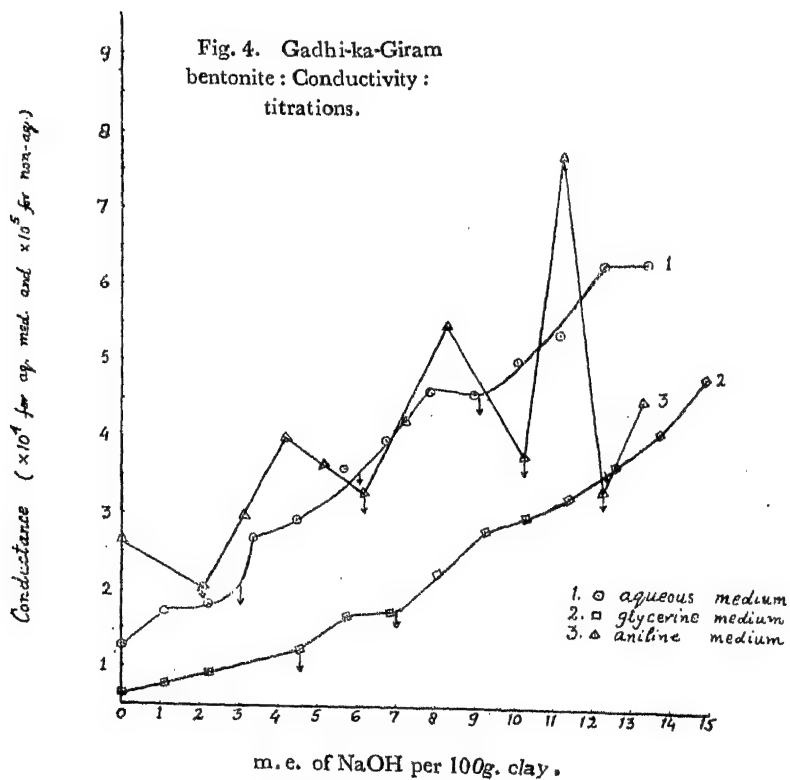
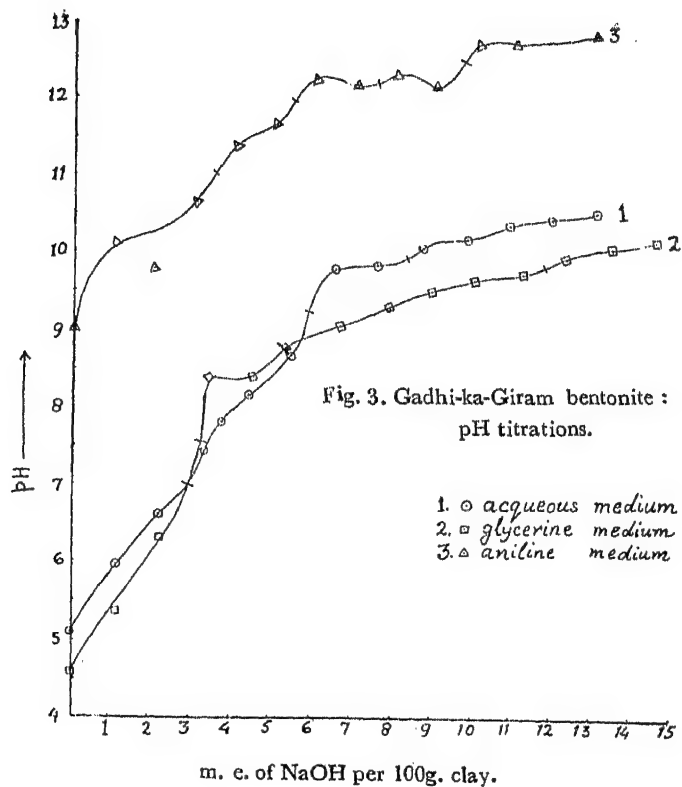


TABLE I
(Akli bentonite)

Medium	B. e. c. in m.e. per 100 g. H. bentonite from pH measurement				pK values			B. e. c. in m.e. per 100 g. H bentonite from conductivity titration breaks		
	At 1st inflexion point	At 2nd inflexion point	At 3rd inflexion point		pK ₁	pK ₂	pK ₃	1st	2nd	3rd
1. Water	52.00 (7.70)	—	—		5.75	—	—	52.00	—	—
2. Water-acetone (1 : 1)	45.00 (7.00)	67.00 (10.00)	—		5.40	6.00	—	46.00	70.00	—
3. Water-glycerine (1 : 1)	53.00 (7.20)	70.65	—		5.35	5.70	—	49.00	66.00	—
4. Aniline non-aqueous	48.00 (9.90)	57.00 (9.35)	71.50 (10.35)		8.10	8.40	8.70	50.00	60.00	75.00

* pH inflexion points are given in brackets.

TABLE II
(Gadhi-ki-Giram bentonite)

Medium	B. e. c. in m.e. per 100 g. H bentonite from pH measurement				PK values				B. e. c. in m.e. per 100 g. H bentonite from conductivity titration breaks			
	At 1st inflexion point	At 2nd inflexion point	At 3rd inflexion point	At 4th inflexion point	pK ₁	pK ₂	pK ₃	pK ₄	1st	2nd	3rd	4th
1. Water	3.00 (7.00)	6.00 (9.20)	8.50 (9.90)	—	6.20	7.00	8.30	—	3.00	6.00	9.00	—
2. Water-glycerine (1 : 1)	3.25 (7.50)	5.75 (8.75)	12.00 (9.80)	—	6.20	7.00	8.90	—	4.50	7.00	12.25	—
3. Aniline non-aqueous	3.60 (11.00)	5.50 (12.00)	7.75 (12.22)	9.95 (12.50)	10.35	10.50	11.35	11.70	2.00	6.00	10.25	12.25

* pH at inflexion points are given in brackets

The conductivity curves (Figs. 2 and 4) although not exhibiting the usual characteristics of ordinary conductometric titration curves (where simple pair of straight lines intersect at the point of equivalence) are, however, of great significance.^{13,17} The appearance of additional breaks is also observed when the conductometric titrations are carried out in the non-aqueous media thereby confirming potentiometric results on bentonites.

In the aqueous medium the 'Akli' sample gives only one inflexion at pH 7.7 (fig. 1, curve 1) while with 'Gadhi-ka-Giram' bentonite three inflexions (at pHs 7.0, 9.2 and 9.9) are obtained (fig. 3, curve 1). Titrations in the non-aqueous media increase the number of inflexions in the case of 'Akli' bentonite (fig. 1, curves 2, 3, 4) while no such effect is observable with the other sample except in case of aniline where a 4th inflexion is obtained at pH 12.5 (fig. 3, curve 3). Besides, the curves for 'Akli' bentonite are more well defined than for the other clay.

Results on b.e.c. (as found from the inflexions from the potentiometric titration curves and the breaks from conductometric curves) provide enough evidence regarding the difference in the composition of the two samples. The occurrence of three inflexions at pH 7.0, 9.2 and 9.9 in aqueous medium and of 4 inflexions in non-aqueous aniline medium suggest the presence of montmorillonite and possibly some other mineral like illite in 'Gandhi-ka-Giram' bentonite.

Such a simple relationship, however, is not obtained, with the 'Akli' bentonite. On the other hand, a fairly high b.e. capacity and the typical monobasic nature of the titration curve in aqueous medium, both point towards the fact that 'Akli' sample is mostly constituted from the mineral montmorillonite. The occurrence of additional inflexions (two in water-acetone and water-glycerine and three in purely non-aqueous aniline) is another point worth considering and may lead to the probable existence of additional clay mineral in Akli bentonite.

Another interesting point emerges out from these investigations, viz, the pK values of the 'Akli' bentonite are lower than those for the other sample which is impure bentonite. Such a behaviour has also been observed by us while studying other soil samples and on the basis of these observations it may be said that a superior quality of bentonite would give lower pK values as obtained from the potentiometric titrations carried out in aqueous or partly aqueous media.

Further work after due removal of free oxides and under carefully controlled conditions of ion saturation (H vs. Al) is in progress and will be communicated shortly.

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NITROSIFICATION IN BENTONITE MEDIUM IN PRESENCE OF AMMONIUM SALTS

By

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ABSTRACT

The process of nitrosification has been studied in bentonite medium in the presence of different ammonium salts. It has been observed that although ammoniacal nitrogen of some ammonium salts is easily converted into nitrite nitrogen in the absence of magnesium or calcium carbonate, the extent of nitrosification depends primarily on the balanced supply of the essential nutrients to the medium. The nature of other cations and anions present in the medium as well as the pH of the medium itself have also a controlling effect on nitrosification. Of the eighteen ammonium salts used, diammonium hydrogen phosphate, ammonium sulphate, ammonium sodium hydrogen phosphate gave maximum nitrosification in bentonite medium.

In our two previous communications (1, 2) we have reported that it is possible to use bentonite as a growth medium for nitrite forming bacteria (*Nitrosomonas*), provided the medium contains optimum amounts of magnesium and calcium carbonates. Other carbonates of divalent metals have been observed to be unsuitable for this medium.

In this paper, we have reported the results obtained on the extent of nitrosification in bentonite medium in the presence of different ammonium salts. The experiments have been performed without adding either magnesium carbonate or calcium carbonate to the medium.

EXPERIMENTAL

The bentonite sample used, was obtained from Kashmir, India. X-ray identification of the clay mineral was originally performed by the Late Dr. S. P. Mitra. The clay mineral was first finely powdered in an agate mortar and then passed through a 100 mesh sieve. The pulverised mineral so-obtained was then stocked in bottles for the experiment.

For the systematic study of the bacterial nitrosification in bentonite medium, each mixture containing 1.0 g. bentonite, an ammonium salt (amount corresponding to 0.02121 g. Nitrogen) and 80 ml. distilled water was taken in a 250 ml. Jena flask and was sterilized in an autoclave for half-an-hour at 15 lbs. pressure. The flasks containing the above medium were left for cooling after sterilization, and were inoculated by 1 ml. of a vigorous culture of the organism diluted with sterilized distilled water. The organism, *Nitrosomonas*, was isolated from a sample of garden soil, details of which have already been given in one of our previous communications (1). The flasks containing the inoculated mixtures and the control sets were incubated at 35° C in an incubator. The nitrite formed in each of the flasks was estimated after the completion of every 48 hours by the Duboscq Colorimeter using 0.5% α -naphthylamine and 0.8% sulphanilic acid in acetic acid (Sp. Gr. 1.04) solution. The growth of the organism was taken to be directly

proportional to the formation of nitrite in the solution. The results reported here are the mean of the two sets which were run side by side.

RESULTS AND DISCUSSION

In one of our previous communications (1), we have reported that nitrosification in bentonite medium is best favoured in the presence of magnesium carbonate, and not in calcium carbonate, the maximum amount of nitrite formation observed in one of the sets at 336 hours being 120.290 mg. The source of ammoniacal nitrogen used was 1 ml. of a 10% solution of ammonium sulphate and the experiments were performed with mixtures, each containing 1.0 g. bentonite, 0.01-0.1g magnesium or calcium carbonates and 80 ml. distilled water. There is thus indication that the conversion of ammonia to nitrite from ammonium sulphate is favoured in the presence of magnesium or calcium carbonate.

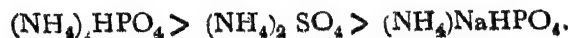
TABLE 1

Nitrosification in Bentonite Medium in presence of Ammonium Salts.

Medium 1.0g. Bentonite + NH_4 salts + 80 ml. distilled water.	Nitrite in mg/Litre						
	Time in hours						
	48	96	144	192	240	288	336
1. Ammonium carbonate	0.7002	0.8100	0.9052	0.9052	1.0500	1.3945	1.8211
2. Ammonium sulphate	0.7500	1.0500	1.5420	3.6980	7.5000	12.9450	28.1620
3. Diammonium Hydrogen phosphate	0.7500	1.0315	2.2230	8.8440	12.6000	17.7690	38.2350
4. Ammonium chloride	0.6563	0.9702	1.4580	2.9180	4.4760	6.9000	21.0000
5. Ammonium bromide	0.6563	0.8844	1.3815	2.4990	3.5000	5.4690	19.3480
6. Ammonium fluoride	0.5834	0.7500	1.3815	2.1000	2.9180	4.5000	12.031
7. Ammonium nitrate	0.8100	0.9702	1.1921	1.6410	2.1000	5.3682	19.3480
8. Ammonium sodium phosphate	0.6563	0.7500	1.0500	1.8750	2.8750	8.8440	32.2360
9. Ammonium thiocyanate	0.5835	0.6029	0.6600	1.3450	1.4580	2.4000	3.8750
10. Ammonium citrate	0.5833

In the present series of experiments none of the above two carbonates was used, and under the above condition the maximum nitrosification observed in 336

hours in the presence of the ammonium salts was 38.2350 mg. of the nitrite. However, the results presented in table 1, clearly show that it is possible to obtain a fairly good growth of Nitrosomonas in bentonite medium even without providing magnesium or calcium carbonate source to the growing bacteria. Here, we may mention that not all the ammonium salts are suitable for the growth of nitrosomonas in bentonite medium, as is evident from table 1 in which the effects of the anions associated are indicated. The best first three ammonium salts, the ammoniacal nitrogen of which can be easily converted into nitrite nitrogen in the bentonite medium inoculated with Nitrosomonas, can be placed in the order



The ammonium salts containing the halides also appear to be good sources of ammoniacal nitrogen for the growing nitrifying bacteria. Incidentally, we may mention that we have not found any nitrite formation in bentonite medium in the presence of citrate, dihydrogen phosphate, oxalate, dichromate, molybdate, acetate, persulphate, arsenate and hydroxide of ammonium. These anions are thus definitely toxic to the growth of nitrosomonas in bentonite medium. However, in the presence of ammonium citrate slight growth of bacteria was observed after a long period; probably it is due to the inhibiting effect of the organic citrate anion, since it is known that organic substances in general retard the growth of nitrifiers.

It is well known (3) that Nitrosomonas grows best in a medium supplied with a source of ammoniacal nitrogen, free calcium or magnesium carbonates, some quantities of phosphate and traces of iron, zinc and copper. A bentonite sample normally contains all these essentials and it thus becomes a good surface for the nitrosification process. The extent of the process is, however, primarily dependent on a balanced supply of these important elements, the pH of the medium and the nature of other cations and anions present. From the results presented in table 1, the importance of these factors is clearly borne out.

ACKNOWLEDGMENT

We express our thanks to the Scientific Research Committee, U. P., for providing a research scholarship to one of the authors (R. C. Rastogi) and thus enabling him to carry on this specific research work.

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AN ELECTROMETRIC AND CONDUCTOMETRIC STUDY OF THE SYSTEMS :

$\text{HgX}_2 - \text{MCN} - \text{H}_2\text{O}$ (where $\text{X} = \text{Cl, Br or CNS}$ and $\text{M} = \text{K or Na}$)

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ABSTRACT

An electrometric and conductometric study of the systems : $\text{HgX}_2 - \text{MCN} - \text{H}_2\text{O}$ (where $\text{X} = \text{Cl, Br or CNS}$ and $\text{M} = \text{K or Na}$) has been carried out and the existence of a number of complexes interpreted.

Although a considerable amount of work¹⁻¹¹ has been done on the complex and mixed halides of mercury, not much systematic work appears to have been carried out on the mixed pseudohalides of the metal. Sherrill and Skowronski¹² have shown the existence of a complex salt $\text{K}_2\text{Hg}(\text{CNS})_4$ by solubility, freezing point and E. M. F. determinations. Corbet¹³ carried out a phase-rule investigation of the system : $\text{Hg}(\text{CN})_2 - \text{KCN} - \text{H}_2\text{O}$. As regards the study of the mixed halide-pseudohalide complexes of mercury, some evidence for the complex ion, $\text{Hg}(\text{CN})_2\text{Cl}^-$ was reported by the ebullioscopic method by Bourion and Rouyer¹⁴. Aggarwal and Mehrotra¹⁵ have recently carried out a conductometric, electrometric and cryoscopic study of the systems : $\text{HgI}_2 - \text{KCN} - \text{H}_2\text{O}$ and $\text{Hg}(\text{CN})_2 - \text{KI} - \text{H}_2\text{O}$ and concluded the existence of the following complexes in solution : $\text{KHg}(\text{CN})_2\text{I}$, $\text{K}_2\text{Hg}(\text{CN})_2\text{I}_2$ and $\text{K}_2\text{Hg}(\text{CN})_4$. Penneman and Jones¹⁶ employing infra-red absorption technique have shown the existence of two complexes i. e., $\text{Hg}(\text{CN})_2\text{Cl}^-$ and $\text{Hg}(\text{CN})_2\text{Cl}^{2-}$ between mercuric cyanide and chloride ions. The authors¹⁷⁻¹⁹ have carried out a preparative study of the systems : $\text{HgX}_2 - \text{MCN} - \text{H}_2\text{O}$ and $\text{Hg}(\text{CN})_2 - \text{MX} - \text{H}_2\text{O}$ (where $\text{X} = \text{Cl, Br or CNS}$ and $\text{M} = \text{K or Na}$) and isolated three different types of complexes : MHgX_2CN , $\text{MHg}(\text{CN})_2\text{X}$ and $\text{M}_2\text{Hg}(\text{CN})_2$ from the potassium systems whereas from the sodium systems the only complex which could be isolated corresponded to the formula $\text{MHg}(\text{CN})_2\text{X}$. The results are summarised in the following table :

Molar ratio of the reaction mixture.	Composition of the product.
1. $\text{HgX}_2 \cdot \text{KCN}$	KHgX_2CN
2. $\text{HgX}_2 \cdot 4\text{KCN}$	$\text{K}_4\text{Hg}(\text{CN})_4$
3. $\text{HgX}_2 \cdot 2\text{KCN}$	$\text{KHg}(\text{CN})_2\text{X}$
4. $\text{Hg}(\text{CN})_2 \cdot n\text{KX}$	$\text{KHg}(\text{CN})_2\text{X}$
5. $\text{HgX}_2 \cdot n\text{NaCN}$	$\text{NaHg}(\text{CN})_2\text{X} \cdot \text{H}_2\text{O}$
6. $\text{Hg}(\text{CN})_2 \cdot n\text{NaX}$	$\text{NaHg}(\text{CN})_2\text{X} \cdot \text{H}_2\text{O}$

$\text{X} = \text{Cl, Br or CNS}$ and $n = 1, 2$ or 4

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In this particular investigation, the authors have carried out an electrometric and conductometric study of the systems: $\text{HgX}_2 - \text{MCN} - \text{H}_2\text{O}$ (where $\text{X} = \text{Cl}, \text{Br}$ or CNS and $\text{M} = \text{K}$ or Na) and interpreted the existence of a number of complexes.

EXPERIMENTAL

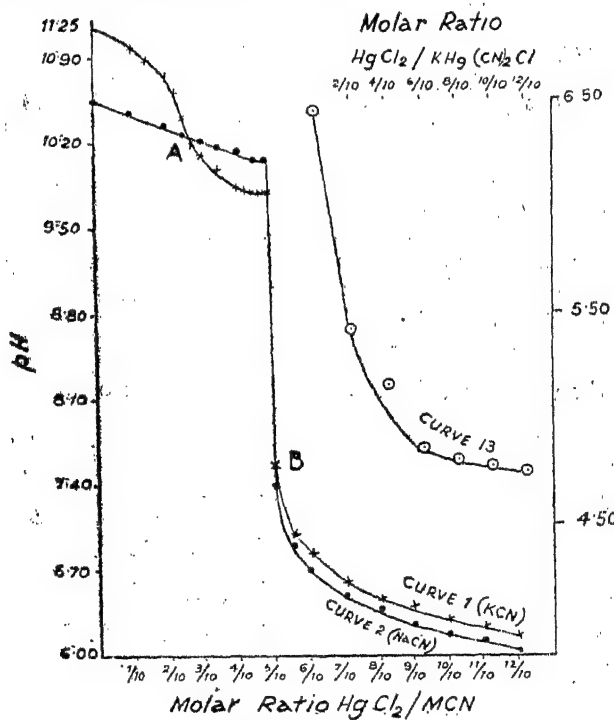
Materials. Mercuric thiocyanate and bromide used were prepared from mercuric nitrate and potassium thiocyanate or bromide, thoroughly washed with distilled water, dried and analysed. Sodium cyanide was an E. Merck product. For all other chemicals, analytical grade reagents were used.

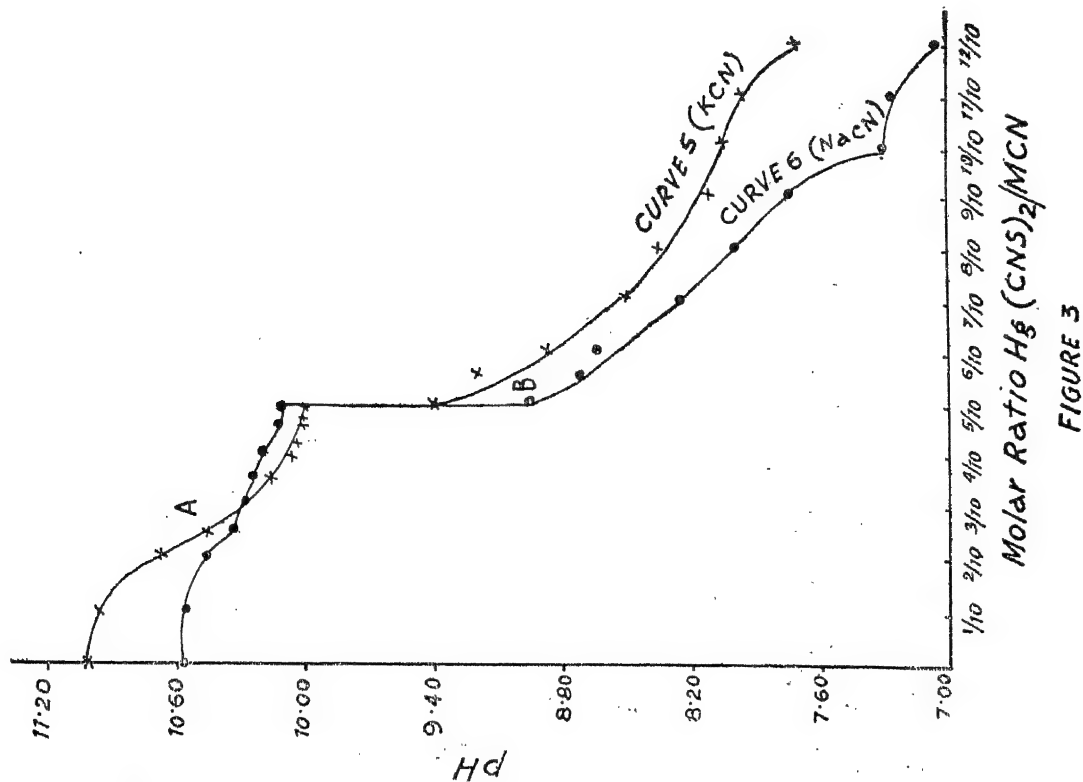
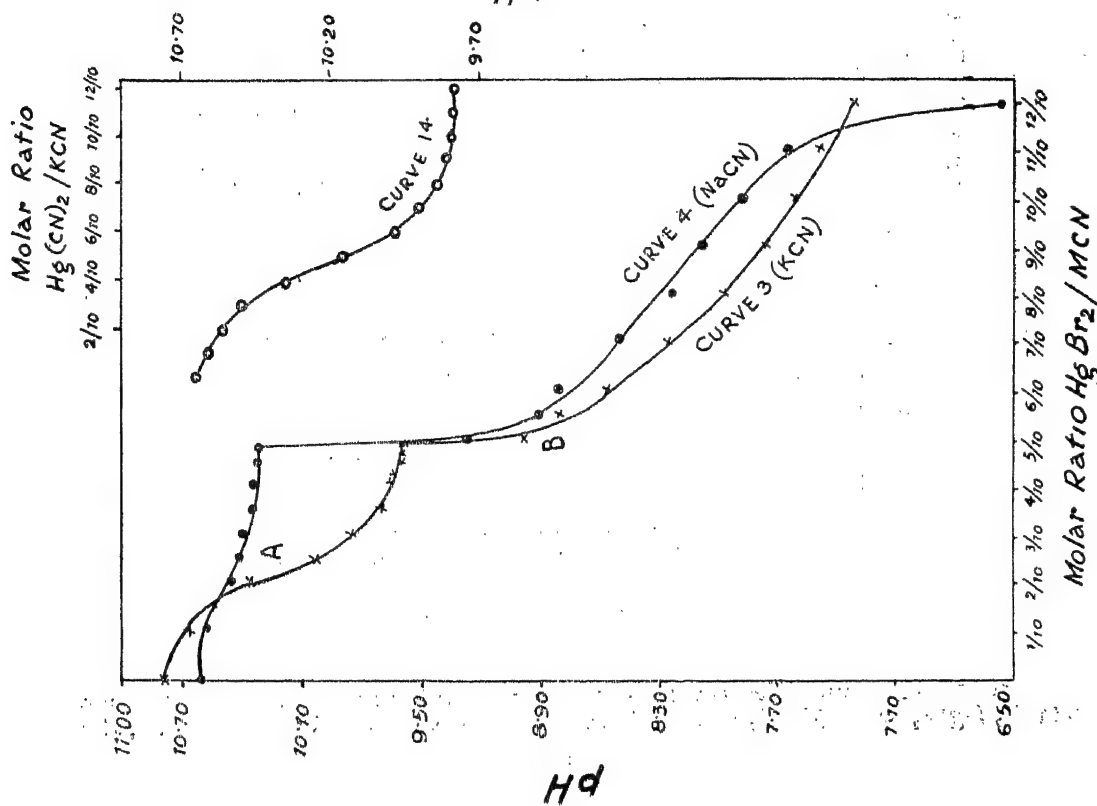
Measurements. A Phillips Direct-reading pH-meter PR 9400 and a Cambridge bench-type pH-meter were employed for electrometric measurements and conductivity was measured with a Phillips Conductivity Measuring Bridge GM 4249 and Leeds Northrup Kohlrausch Slidewire No. 4258.

Techniques and Conditions. A series of solutions were prepared by the monovariation method i. e., by keeping the concentration of one of the components (MCN) constant (10 ml. of molar solution) and varying that of the other (HgX_2). Each solution was made upto 100.00 ml. with conductivity water and allowed to stand overnight in order to ensure the establishment of the equilibrium.

RESULTS AND DISCUSSION

The results obtained are plotted in Figs. 1-4.





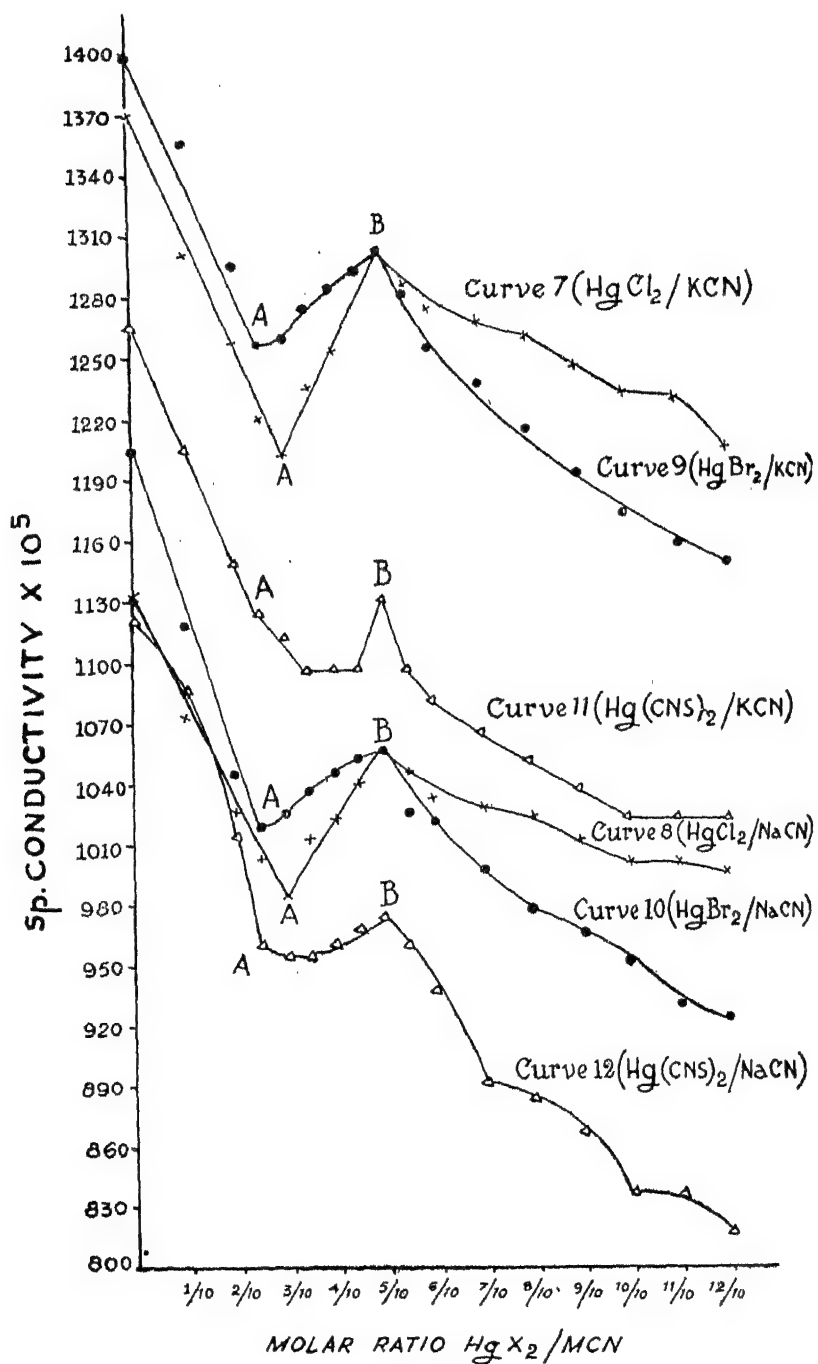
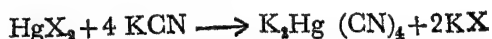


FIGURE 4

pH Measurements. The curves 1—6 show that till the ratio of mercuric halide (HgCl₂, HgBr₂ or Hg(CNS)₂) and alkali cyanide (KCN or NaCN) becomes 1 : 2, the

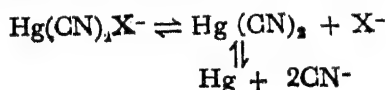
pH gradually decreases as the amount of the mercuric compound increases. This may be attributed to be due to the gradual conversion of highly alkaline alkali cyanide into almost unionised mercuric cyanide. However, in case of potassium systems an earlier inflexion point A is obtained where the molar ratio of mercuric halide and potassium cyanide is 1 : 4. This can be explained on the basis of the reaction.



The complex $\text{K}_4\text{Hg}(\text{CN})_4$ has actually been isolated from the reaction mixtures with the above molar ratio whereas in case of sodium systems no such compound could be isolated. Further confirmation for this has been obtained from a study of the system : $\text{Hg}(\text{CN})_2 - \text{KCN} - \text{H}_2\text{O}$ (curve 14) which gives a similar inflexion point when the molar ratio of mercuric cyanide and potassium cyanide is 1 : 2. This inflexion point can also be observed in case of the system : $\text{Hg}(\text{CNS})_2 - \text{NaCN} - \text{H}_2\text{O}$ but is not well-marked in case of other sodium systems.

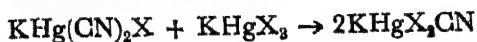
When the ratio of mercuric halide and alkali cyanide becomes exactly 1 : 2, there is a sudden fall in pH due to the conversion of all the alkali cyanide into almost unionised mercuric cyanide which as evinced by our preparative studies takes up one mole of the alkali halide forming $\text{MHg}(\text{CN})_2\text{X}$. This corresponds to the inflexion point B.

Again, the pH slowly decreases as the addition of more mercuric halide suppresses the secondary ionisation of $\text{Hg}(\text{CN})_2\text{X}^-$



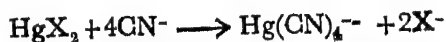
This has been confirmed from a study of the system :

$\text{HgCl}_2 - \text{KHg}(\text{CN})_2\text{Cl} - \text{H}_2\text{O}$ (curve 13) when similar results were obtained. Further, in case of potassium systems the possibility of the following reactions cannot be neglected.

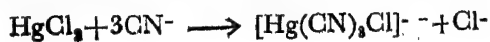


as the complexes KHgX_3CN have actually been isolated, although the inflexion point at the molar ratio HgX_2 . KCN is not very distinct.

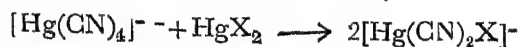
Conductivity Measurements. The curves 7-12 show that the conductivity first decreases as the amount of added mercuric compound increases and an inflexion point A is obtained when the molar ratio of mercuric halide and alkali cyanide is 1 : 4. This may be attributed to the formation of the complex $\text{Hg}(\text{CN})_4^{--}$ ions, the mobility of which can be well expected to be lower than that of the cyanide ions.



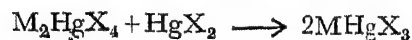
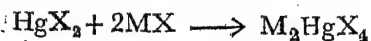
Further, in case of chloride systems the inflexion point A occurs when the molar ratio of mercuric halide and alkali cyanide is approximately 1 : 3. This may be explained on the basis of the formation of $[\text{Hg}(\text{CN})_3\text{Cl}]^-$ - the existence of which has been shown by Penneman and Jones¹⁶ also.



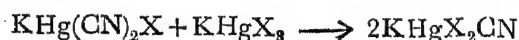
On further addition of the mercuric compound, the conductivity shows a tendency to increase and maxima (B) are obtained when the molar ratio of mercuric halide and alkali cyanide is 1 : 2 corresponding to the formation of $\text{MHg}(\text{CN})_2\text{X}$. The replacement of $[\text{Hg}(\text{CN})_4]^-$ anions by two $[\text{Hg}(\text{CN})_2\text{X}]^-$ anions would be the cause of this increase in conductivity :



Further decrease in conductivity may be assigned to the complexation reactions between the added mercuric compound and the free alkali halide formed in the solution from earlier reactions :



In case of potassium systems, due to the isolation of compounds of the type KHgX_2CN on the preparative side, the possibility of another reaction is also to be accounted for,



although the inflexion point at the molar ratio $\text{HgX}_2 \cdot \text{KCN}$ is not very distinct indicating weak complexation.

One of us (A. K. A.) is grateful to C. S. I. R., New Delhi for a Junior Research Fellowship during the tenure of which the above work was carried out.

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SOIL MOISTURE SYSTEM : MOVEMENT OF MOISTURE AND SALT IN AN UNSATURATED PHASE, PART I

By

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ABSTRACT

The results of soil moisture experiments conducted in the unirrigated profiles having varying water table conditions indicate positive and highly significant correlations between the natural moisture content and clay and clay plus silt content of soils. The profiles attain a sort of natural moisture equilibrium, which is disturbed only by irrigation or fluctuations in climatic elements. The correct programme of land reclamation can, therefore, be chalked out on the basis of soil moisture system of the profiles.

A soil in order to carry out the function of plant growth must contain a certain amount of water and the movement of this water takes place through the soil pore-space. Water may move in soils under any one of the following conditions, either alone or in combination :—

1. Gravity.
2. Capillarity.
3. Vapour Phase.

A simple mathematical derivation of the theory of the movement of moisture under unsaturated conditions based on the potential gradient has been developed by Dhawan and Malhotra (3) where

$$K = \frac{1 - P}{1 + P} \cdot \frac{S^2}{T}$$

Where K = Constant depending upon the type of soil and state of compaction etc.

S = Thickness of the Soil.

P = Variation in moisture content.

T = Time.

A soil profile consists of different horizons possessing soils of variable physico-chemical characteristics. Due to the existence of different types of soils at varying depths, a dynamic equilibrium is bound to be set up as regards their moisture content. It was, therefore, thought feasible to further elucidate this phenomenon by investigating the moisture equilibrium of a large number of profiles upto water table, taken from different areas having variable water table conditions in order to determine the respective role of clay, silt and sand on the moisture holding capacity of these soils in unirrigated zones. Secondly laboratory experiments were carried out to investigate the moisture content of different types of soils at which capillary permeability becomes zero.

EXPERIMENTAL

(a) The following two studies were conducted :—

I. Moisture equilibrium in Unirrigated Profiles.

Soil profiles down to the water table were taken from different un-irrigated areas and analysed for the following soil constants :—

- (i) Natural Moisture Percentage.
- (ii) Mechanical Analysis.
- (iii) Total Soluble Salt Content.

The results of the above investigations were examined in order to study the relation between the different size particles and the natural moisture content of the soils and to see how the movement of salt was affected in different horizons due to the variation in their mechanical analysis.

II. Determination of Moisture content at which capillary permeability is zero.

(a). A typical Punjab soil containing about 7.0 per cent clay was dried, powdered and passed through 60, 100, 170 and 300 mesh B. S. sieve. A known amount of moisture was added and the soil was well mixed in order to have a uniform moisture all round. The moisture content of the soil was determined and it was compacted to a dry bulk density of 1.5 in a glass tube of about 1.0 inch diameter and 6.0" long, while in another similar glass tube sand was compacted at the same density. The variation in moisture content of soil and sand was varied from about 5% to about 20%. First the moisture content of the soil was kept near about 5.0 per cent and the moisture content of the sand was increased from about 5.0 per cent to about 20 per cent. In the second set the moisture content of the soil was increased from 5.0 % to about 20.0 percent while the moisture content of the sand was kept at about 5.0 percent. The two tubes were placed face to face making a complete contact. All the sides were waxed throughly to prevent any loss of moisture due to evaporation. The tubes were kept in the horizontal position for seventy two hours, after which they were separated and moisture estimation was carried out. The gain or loss of moisture in the soil and sand was determined and the moisture content at which capillary permeability stopped was calculated for different percentages of moisture for soil and sand respectively. The mechanical analysis of soil passing (60, 100, 170 and 300) mesh sieve is given below :—

TABLE I

Mechanical analysis of soil passing (60, 100, 170 and 300 Mesh sieve (B. S.))

	1	60	100	170	300
1. Clay (particles below 0.002 mm) ...		6.80	7.40	7.90	8.20
2. Fine silt (particles greater than 0.002 mm but less than .01 mm) ...		5.20	7.00	9.50	13.10
3. Coarse silt (particles greater than 0.02 mm but less than 0.02 mm) ...		7.90	11.20	13.50	20.0
4. Fine sand (particles greater than 0.02 mm but less than 0.2 mm) ...		48.00	70.10	69.02	58.39
5. Coarse sand (particles greater than 0.02 mm but less than 2.0 mm) ...		32.10	4.30	0.08	0.11

Particle size Distribution

S. No.	Mesh No. B. S.	Percentage Retained
1.	7	0.0%
2.	10	0.0%
3.	36	7.3%
4.	60	36.0%
5.	72	7.2%
6.	100	30.2%
7.	120	14.9%
8.	150	3.9%
9.	Passing 150	0.5%

Discussion of Results "Diagrammatic Representation of Analytical Results."

To facilitate the comparison between the natural moisture content and the clay, silt and sand content of soils, the results of analysis have been represented graphically in Fig. I-III.

Fig. I. Relation between clay and moisture retained (in profiles).

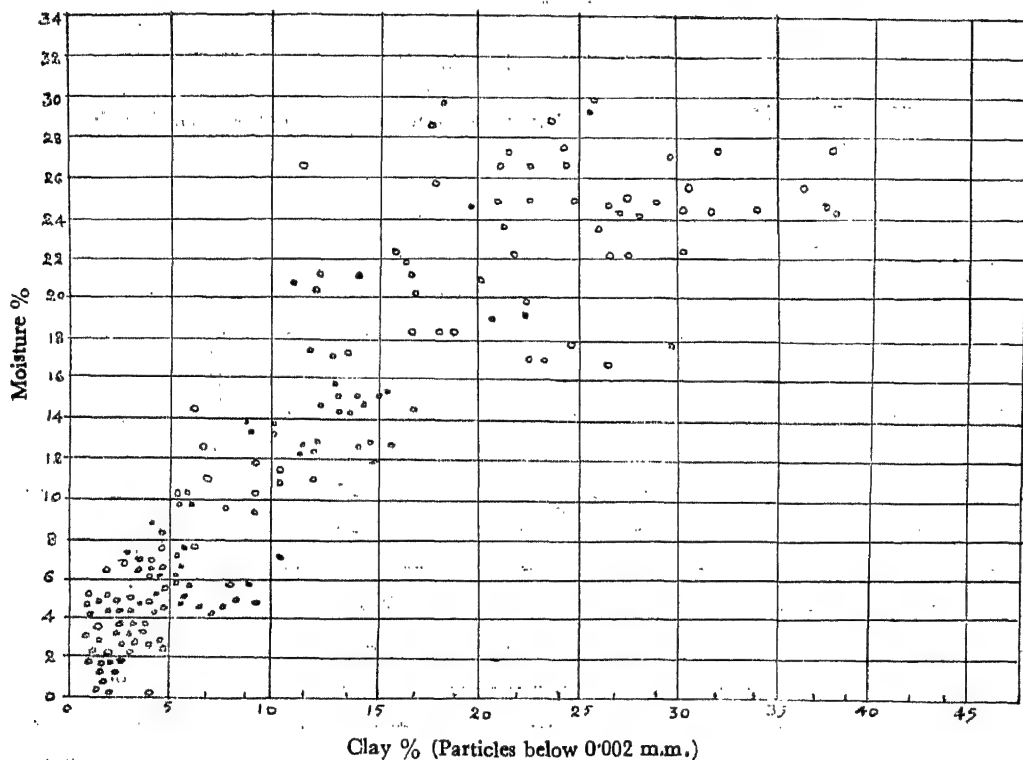


Fig. II. Relation between clay plus silt and moisture retained (in Profiles).

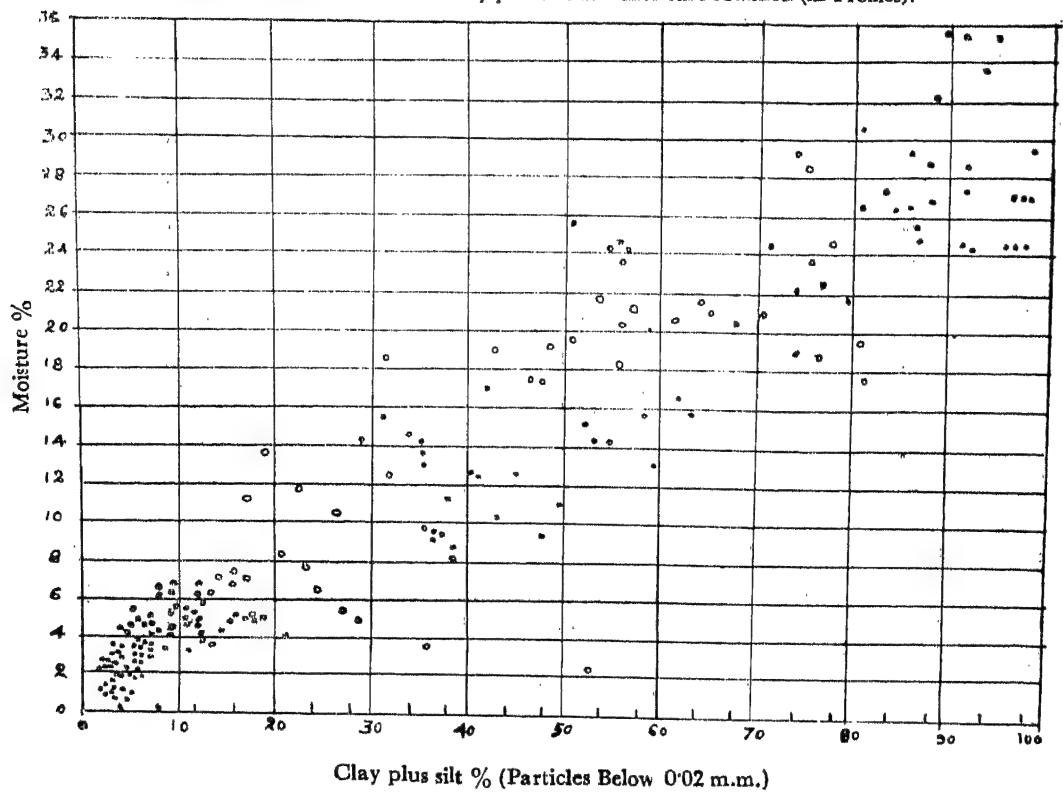
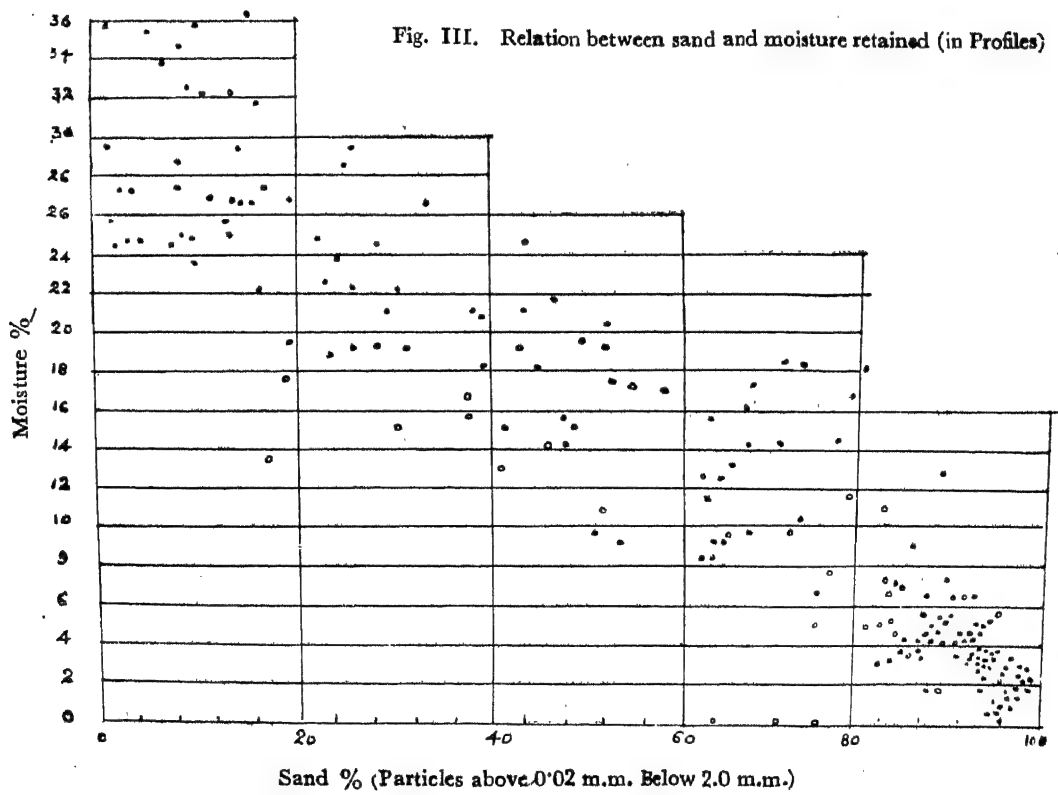


Fig. III. Relation between sand and moisture retained (in Profiles)



Statistical treatment of Analytical Results.

An examination of the Figs. I-III brings out diagrammatically a sort of relationship between the natural moisture content and clay, clay plus silt and sand content of soils. In calculating the correlation coefficients, the top ten to fourteen feet of the soils and four feet of the soil from water table upward were left out. The former was under the influence of pellicular zone and the latter under capillarity. Asghar and Dhawan (2) investigated in detail the formation of pellicular zone in different types of soils. They observed that the depth upto which the effect of evaporation was noticeable ranged from 10.0 ft to 14.0 ft, depending upon the nature of the soil. This depth increased with the decrease in clay content.

- Variable 1. = Natural moisture content.
 Variable 2. = Clay percentage (Particles below 0.002 mm.
 or = Clay plus silt percentage.
 Particles below 0.02 mm.
 or = Sand percentage Particle above 0.02 mm. but less than
 2.0 mm.)
 Y 1,2 = Total correlation between variable 1 & 2.

TABLE II

Correlation between natural moisture content and clay, clay plus silt and sand content of soils

S. No.	Size Particle	No. of observations	r 1,2	Remarks.
1.	Clay percentage	225	+ 0.9016	Significant
2.	Clay plus silt percentage	225	+ 0.9255	do.
3.	Sand Percentage	225	- 0.9255	do.

The respective regression equations are given below :—

$$r = 0.85x + 2.26$$

$$r = 0.279 x_1 + 1.97$$

Where

r = Natural Moisture content.

x = Clay percentage.

x_1 = Clay plus silt percentage.

All the above correlations are highly significant. The correlations with clay and clay plus silt are positive and significant. It shows that the higher the percentage of clay or clay plus silt, the greater is the moisture holding capacity of the soils. With the increase in sand content, the correlation becomes negative and

consequently the retentivity of moisture becomes comparatively less. A sort of moisture equilibrium is reached between the different horizons. Further movement of moisture or salt is automatically stopped.

An example of the equilibrium stage of the movement of moisture and salts in an unirrigated soil profile is cited below :—

TABLE III

Water table profile taken from village Shahpur Begu District Hissar
Punjab India

S. No.	Regd. No.	Depth in ft.	Natural Mois- ture %	Total salt %	Clay %	Silt %	Sand %
1.	56284	18	9.9	0.21	11.1	49.75	25.15
2.	56285	19	22.2	0.31	21.9	52.10	26.00
3.	56286	20	16.7	0.31	26.7	35.6	37.7
4.	56287	21	12.7	0.32	14.8	25.6	59.6
5.	56288	22	17.5	0.30	12.0	34.3	54.2
6.	56289	23	22.0	0.32	13.8	56.3	32.9
7.	56290	24	26.6	0.38	11.5	69.3	18.2
8.	56291	25	21.7	0.34	16.3	47.7	36.0

The top seventeen feet of the above profile are sandy (sand more than 80.0% and the salt concentration is less than 0.15 percent), which clearly indicates that there is no danger of the rise of salts in such type of profiles. It is very interesting to find that from 29th ft. to 56 ft. depth, the salt concentration is below 0.15 % as the sand content is above 80.0 %. From 56 to 59 feet depth the variation in moisture percentage, total salts and the clay, silt and sand percentage are as follows.

S. No.	Regd. No.	Depth in ft.	Moisture %	Total Salt %	Clay %	Silt %	Sand %
1.	56322	56	19.1	0.80	18.0	50.2	31.8
2.	56323	57	14.1	0.48	20.5	38.9	39.6
3.	56324	58	16.0	0.60	25.0
4.	56325	59	15.2	0.60	14.6	37.3	48.1

The moisture content above 56 ft. depth is below 5.0 percent. The results of the above table confirm that in unirrigated areas a sort of equilibrium is established as regards the retention of moisture and total salts. In these areas, where the top is comparatively sandy as compared with the underlying layers, there is very little chance of the formation of saline soils. Therefore a detailed soil survey is necessitated for demarcating those zones, which are not amenable to a saline formation. Such advanced information will go a long way in chalking out the programme of land improvement.

II. Determination of Moisture Equilibrium at which the capillary permeability is zero.

The second experiment sought to determine the comparative moisture content of soil and sand at which there was no transference of moisture or salt. Eight sets of glass tubes as described under the caption "Experimental" were half filled with soil, containing about 7% clay and half with sand. Both the soil and sand were kept at the same moisture content varying from 5% to about 20.0%. After seventy two hours the soil and sand samples were taken for moisture estimation. It was inferred that the moisture content at which the capillary permeability was zero was 17.25 per cent. This meant that no salt movement could take place from the sand to the soil if the moisture content of both soil and sand was 17.25 per cent.

The results of the above experiment were further confirmed by taking glass tubes 12" long and the following sets were prepared.

1st Set.

- Top 4" = Soil containing 1.0% Na_2SO_4 .
- Middle 4" = Sand.
- Bottom 4" = Soil.

IInd Set.

- Top 4" = Soil.
- Middle 4" = Sand containing 1.0% Na_2SO_4 .
- Bottom 4" = Soil.

IIIrd Set.

- Top 4" = Soil.
- Middle 4" = Sand.
- Bottom 4" = Soil containing 1.0% Na_2SO_4 .

The moisture content of the whole tube was maintained from 5.0% to 20.0 per cent. Both the ends of the tubes were properly waxed in order to avoid any evaporation. Twelve such sets of tubes were kept, three for 5.0 %, three for 10.0 %, three for 15.0% and three for 20.0% moisture content. Soil and sand samples were taken after seventy-two hours and analysed for moisture and salt content. It was observed that the salt movement took place only from sand to the soil portion upto 15.0 moisture content. When the moisture content of the soil and sand portions

was kept at 18.%, the movement of salt took place from the top soil to the lower layers of sand and soil. Even some movement of salt was observed from the bottom layer of soil to the sand portion. This means that when the field capacity *i.e.* the maximum water holding capacity of the soil is satisfied, there is likelihood of the movement of moisture and salts taking place from the soil to the sandy horizon. Therefore, it is very necessary to know before hand the conditions under which the movement of moisture and salt can take place from the saline subgrade upwards through the sandy carpet over laid for the prevention of the upward rise of salts. Asghar and Dhawan (2) had investigated the same effect with a soil containing about 17.0 % clay.

III. Experiments were next conducted to study the moisture content at which the capillary permeability becomes zero at different moisture contents in the soil sand moisture system. The detailed technique of the experiment has been discussed under "Experimental". The following were the broad conclusions drawn from the above study.

(a). No movement of moisture took place from the soil to the sand upto about 15.0%. (b) The movement of moisture from the soil to the sand made its way as follows :—

TABLE IV

Moisture content of the soil and sand at which movement of moisture tookplace

S. No.	Soil Type	Initial moisture content %		Final Moisture Content %	
		Soil	Sand	Soil	Sand
1.	Soils passing 60 mesh.	... 18.7%	3.5%	15.8%	5.8%
2.	Soil passing 100 mesh.	... 19.5%	4.8%	17.6%	7.2%
3.	Soil passing 120 mesh.	... 18.8%	4.0%	18.9%	4.9%
4.	Soil passing 300 mesh.	... 19.4%	4.6%	19.5%	4.0%

A glance at the above table shows that in finer soil, the higher was the moisture content at which it could release moisture to the sandy stratum. This shows that the surface area of the soils is mainly responsible for the determination of the direction, rate and the extent of the moisture movement.

The above results were further confirmed by studying the movement of different sodium salts from the sand to soil at moisture contents varying from 5% to 15%.

Ten inches long pyrex glass tubes of about one inch internal diameter were half filled with sand and the other half with soil containing clay 14.4%, Silt, 27.8% and sand 57.87%. Different proportions of sodium salts i.e. sodium sulphate, sodium chloride and sodium carbonate were added only in sand. The moisture content was kept same in both the sand and soil.

The tubes were sealed at both the ends. A pin hole was made at the sealed end of the soil. The salt percentage was 1.5% and the respective concentrations in the different sets were as follows :—

Sodium Sulphate	...	0.5%	0.75 %	0.375%	0.375%
Sodium Chloride	...	0.5%	0.375%	0.75 %	0.375%
Sodium Carbonate	...	0.5%	0.375%	0.375%	0.75 %

The sealed tubes were kept for seventy two hours, after which samples were taken from the sand and soil portions for the estimation of individual salts. In table VI are presented the comparative percentages of the sodium salts moved to the soil and remained in the sand. A moment's reflection at the table VI reveals that the highest percentage of salt had moved in those sets, containing 10.0% original moisture content. Secondly there was no preferential movement of any individual salts.

The interesting observation noticed was that the minimum movement of salts took place, when the soil sand system was at 15.0% moisture content. The results of moisture content both in the soil and sand portions after seventy two hours are given below :—

TABLE V
Comparative Moisture content in soil-sand system after 72 hours

S. No.	Type of Stratum	Initial moisture content %	Final Moisture content after 72 hours %
I	Sand	15.0	13.85
	Soil	15.0	15.80
II	Sand	15.0	14.10
	Soil	15.0	18.20
III	Sand	15.0	14.30
IV	Soil	15.0	15.60
IV	Sand	15.0	14.50
	Soil	15.0	15.70
V	Sand	10.0	6.85
	Soil	10.0	15.02

TABLE VI

Showing comparative movement of Sodium Carbonate, Sodium Chloride and Sodium Sulphate in Sand and Soil System at varying Moisture contents after 72 hours

Total Salts Added = 1.5%

S. No.	Concentration of Individual salts in sand added (Percentage) Sodium Salt	Moisture % in sand & Soil system	Type of stratum	After 72 hours		
				Sodium Carbonate %	Sodium Chloride %	Sodium Sulphate %
1.	Sulphate 33%	...	15.0	Sand	17.0	24.5
	Carbonate 33%				16.3	17.0
	Chloride 33%	...	15.0	Soil	8.8	16.0
2.	Sulphate 50%	...	15.0	Sand	14.3	29.3
	Carbonate 25%				10.7	35.4
	Chloride 50%	...	15.0	Soil	5.7	14.6
3.	Sulphate 25%	...	15.0	Sand	11.5	40.15
	Carbonate 25%				13.5	13.8
	Chloride 50%	...	15.0	Soil	9.85	11.2
4.	Sulphate 25%	...	15.0	Sand	33.1	20.0
	Carbonate 50%				16.9	13.0
	Chloride 25%	...	15.0	Soil	5.0	12.0
5.	Sulphate 33%	...	10.0	Sand	15.6	15.9
	Carbonate 33%				17.5	16.8
	Chloride 33%	...	10.0	Soil	17.4	16.5
6.	Sulphate 50%	...	10.0	Sand	12.5	15.8
	Carbonate 25%				12.5	26.11
	Chloride 25%	...	10.0	Soil	9.2	26.11
7.	Sulphate 25%	...	10.0	Sand	11.8	26.4
	Carbonate 25%				13.2	12.7
	Chloride 50%	...	10.0	Soil	23.6	12.3
8.	Sulphate 25%	...	10.0	Sand	25.0	11.8
	Carbonate 50%				25.0	11.2
	Chloride 25%	...	10.0	Soil	13.2	14.8
9.	Sulphate 33%	...	5.0	Sand	17.2	19.1
	Carbonate 33%				16.1	20.9
	Chloride 33%	...	5.0	Soil	14.2	12.4
10.	Sulphate 50%	...	5.0	Sand	13.9	15.4
	Carbonate 25%				11.1	34.4
	Chloride 25%	...	5.0	Soil	9.6	15.6
11.	Sulphate 25%	...	5.0	Sand	33.8	15.0
	Carbonate 50%				16.2	15.3
	Chloride 25%	...	5.0	Soil	10.0	9.7
12.	Sulphate 25%	...	5.0	Sand	14.5	31.5
	Carbonate 50%				10.5	14.0
	Chloride 50%	...	5.0	Soil	18.49	11.0

VI	Sand	10.0	4.57
	Soil	10.0	15.37
VII	Sand	10.0	5.04
	Soil	10.0	15.43
VIII	Sand	10.0	5.42
IX	Sand	5.0	3.09
	Soil	5.0	7.20
X	Sand	5.0	3.09
	Soil	5.0	7.74
XI	Sand	5.0	3.05
	Soil	5.0	7.63
XII	Sand	5.0	3.02
	Soil	5.0	7.91

It was inferred from the results of the above experiment that the minimum movement of moisture was held in the set placed at 15.0% moisture content and the maximum movement of moisture took place in the system containing 10.0% moisture content.

It is an accepted fact that the movement of salts is governed by the movement of moisture. As the movement of moisture at 15.0 per cent was minimum, hence the movement of salts was also minimum at this moisture content. It, therefore, indicates that near about this moisture content the capillary permeability was approaching zero value, hence the movement of salts was minimum. These results further lend support to the idea that with soils of varying mechanical composition when placed in contact with each other, no further movement of moisture or salts takes place if the original moisture of both the horizons is near about the moisture content at which the capillary permeability becomes zero.

The results of the above investigation need to be applied in framing a programme of land improvement. Land improvement does not consist only in the reclamation of deteriorated lands, but also in maintaining its original fertility. The main factor governing these operations is the soil moisture system. Definite irrigations are to be given to see that the whole of the salt is completely removed from the profile and a proper crop-rotation is to be recommended, which may not produce such type of moisture equilibrium, causing rise of salts. Hence it is very essential that special importance should be given to the soil moisture system of the soil profiles to be taken up for land improvement. It does not need any emphasis to say that faulty irrigation cum agricultural practices have been greatly responsible for the formation of saline soils.

SUMMARY

The following conclusions were drawn from the above investigation :—

- (i) Positively highly significant correlations were found out between the natural moisture content any clay and (clay plus silt content) of soils in unirrigated profiles.

- (ii) A sort of moisture-equilibrium is established between the different horizons of the soil profiles, which is disturbed only by rainfall, irrigation or fluctuations in climatic elements. The disturbance in the moisture equilibrium initiates salt movement.
- (iii) The moisture and salt movement are stopped between the adjacent horizons, when their capillary permeability becomes zero.
- (iv) The moisture content at which the capillary permeability of soils becomes zero depends on the structure etc. and their comparative moisture content.
- (v) The finer the soil, the greater is its capacity of the retention of moisture content above which it can release moisture to the sandy soil. This shows that the specific surface of the soils may be responsible for the determination of the direction, rate and the extent of the moisture movement.
- (vi) When the mixture of sodium salts *i.e.* sodium sulphate sodium chloride and sodium carbonate are present in the soil, there is no preferential movement of any individual salts.
- (vii) For successfully carrying out the programme of land improvement, a true knowledge of soil-moisture system of the profiles is very essential, before one can recommend the correct type of crop-rotation and other measures.

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A FEW EXAMPLES SHOWING USE OF HYPO-ELASTICITY IN PLASTICITY

By

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ABSTRACT

Two problems, solid rotating shaft and pure shear under loading, have been discussed without using any approximation to illustrate the use of hypo-elasticity in plasticity.

1. INTRODUCTION

A general theory of work-hardening incompressible plastic materials has been developed by Green¹ as a special case of Truesdell's² theory of hypo-elasticity. Equations have been obtained for a single loading followed by one unloading and attention has been drawn to materials for which the stress logarithmic strain curve for unloading in simple extension is linear. Using a particular case of the corresponding constitutive equations for loading, which is a generalisation of that suggested by Prager³ applications have here been made to a couple of problems viz. a solid rotating shaft and pure shear. We are able to solve the constitutive equations without using any approximation. For large values of α , which is generally the case, we find that the transition from elastic to plastic region is gradual as in simple extension and that the approach to the yield stress is extremely rapid. The stress reaches the yield value for quite small values of strain.

2. BASIC EQUATIONS

The constitutive equations for loading, as established by Green¹, for incompressible hypo-elastic materials exhibiting the work-hardening property are as follows :

$$\dot{t}_{ij}^i = d_{ij}^i + t_{im}^i d_{ij}^m - t_{jm}^m d_{im}^i - \frac{2}{3} \alpha^2 M t_{ij}^i, (M \geq 0), \quad (2.1)$$

where

$$\dot{t}_{ij}^i \equiv \frac{\partial}{\partial t} t_{ij}^i + v^m \frac{\partial t_{ij}^i}{\partial x^m} + t_{im}^i \frac{\partial v^m}{\partial x^j} - t_{jm}^m \frac{\partial v^i}{\partial x^m}, \quad p \equiv -\frac{1}{3} s_r^r,$$

$$t_{ij}^i = s_{ij}^i - \frac{1}{3} s_{ij}^i s_r^r, \quad M \equiv t_{ij}^i d_{ij}^j,$$

and d_{ij}^i is the rate of deformation tensor.

The equations of motion are

$$2\mu s^{ij},_{j} + \rho F^i = \rho \left(\frac{\partial s^i}{\partial t} + s^m v^i_{,m} \right), \quad (2.2)$$

where F^i is the body force vector per unit mass, the comma denotes covariant derivative and μ is the shear modulus. We are taking twice the shear modulus as the unit of stress.

The equation of mass is

$$v^i_{,i} = 0 \quad (2.3)$$

where v^i is the contravariant velocity field.

3. SOLID ROTATING SHAFT UNDER SIMPLE EXTENSION

Referred to fixed cylindrical system of coordinates, we take the physical components of the velocity field as mentioned below:

$$u = A r \dot{\epsilon}, v = r \omega \dot{\epsilon}, w = -2A z \dot{\epsilon}, \quad (3.1)$$

where A is a given constant, ω is the constant angular velocity of the shaft and ϵ is a function of time to be determined. The rate of deformation tensor becomes

$$d^i_j = \begin{bmatrix} A\dot{\epsilon} & 0 & 0 \\ 0 & A\dot{\epsilon} & 0 \\ 0 & 0 & -2A\dot{\epsilon} \end{bmatrix} \quad (3.2)$$

We assume the extra-stress tensor in the form

$$t^i_j = \begin{bmatrix} t^1_1 & 0 & 0 \\ 0 & t^2_2 & 0 \\ 0 & 0 & t^3_3 \end{bmatrix},$$

$$\text{so that } t^1_1 + t^2_2 + t^3_3 = 0, \quad (3.3)$$

and where t^1_1, t^2_2, t^3_3 are functions of r, t and z .

From (3.2) and (3.3), we have

$$M = 3A\dot{\epsilon} (t^1_1 + t^2_2) \quad (3.4)$$

Now out of the equations (2.1) to (2.3) some reduce to

$$\frac{1}{A\varepsilon} \frac{\partial}{\partial t} t_1^1 + r \frac{\partial}{\partial r} t_1^1 - 2z \frac{\partial}{\partial z} t_1^1 = 1 + 2 \alpha^2 t_1^1 t_3^3, \quad (3.5)$$

$$\frac{1}{A\varepsilon} \frac{\partial}{\partial t} t_2^2 + r \frac{\partial}{\partial r} t_2^2 - 2z \frac{\partial}{\partial z} t_2^2 = 1 + 2 \alpha^2 t_2^2 t_3^3, \quad (3.6)$$

$$\frac{1}{A\varepsilon} \frac{\partial}{\partial t} t_3^3 + r \frac{\partial}{\partial r} t_3^3 - 2z \frac{\partial}{\partial z} t_3^3 = -2 + 2\alpha^2 (t_3^3)^2, \quad (3.7)$$

$$\frac{\partial}{\partial r} t_1^1 + \frac{1}{r} (t_1^1 - t_2^2) - \frac{\rho}{2\mu} r \left\{ A\varepsilon + \varepsilon^2 (A^2 - \omega^2) \right\} = \frac{\partial p}{\partial r}, \quad (3.8)$$

$$\frac{\partial}{\partial z} t_3^3 - \frac{\rho}{\mu} z A (2A\varepsilon^2 - \varepsilon^2) = \frac{\partial p}{\partial z}, \quad (3.9)$$

while others are identically satisfied.

Solution of (3.7) gives

$$t_3^3 = \frac{1}{\alpha} \tanh \left[2 \alpha \left\{ \phi \left(r e^{-A\varepsilon}, z e^{2A\varepsilon} \right) - A\varepsilon \right\} \right], \quad (3.10)$$

where ϕ is an arbitrary function.

If we look at the equation (3.8) keeping the finiteness of stress at $r = 0$ in view, then we can, without any loss of generality infer from (3.5) and (3.6) that

$$t_1^1 = t_2^2$$

Therefore from (3.3) and (3.10) we can say that

$$t_1^1 = t_2^2 = \frac{1}{2\alpha} \tanh \left[2 \alpha \left\{ A\varepsilon - \phi \left(r e^{-A\varepsilon}, z e^{2A\varepsilon} \right) \right\} \right], \quad (3.11)$$

which does satisfy (3.5) and (3.6) leaving ϕ still undetermined.

Integrating equation (3.8) partially w. r. t. 'r' and observing that

$$t_1^1 = t_2^2 \text{ we get}$$

$$s_1^1 = t_1^1 - p = \frac{\rho r^2}{4\mu} [A\varepsilon + \varepsilon^2 (A^2 - \omega^2)] + F(z, t), \quad (3.12)$$

where $F(z, t)$ is another arbitrary function.

Since $s_1^1 = 0$ at $r=a$, we must have :

$$F(z, t) = \frac{\rho}{4\mu} a^2 [A\ddot{\varepsilon} + \dot{\varepsilon}^2 (A^2 - \omega^2)],$$

and hence

$$s_1^1 = \frac{\rho}{4\mu} (r^2 - a^2) [A\ddot{\varepsilon} + \dot{\varepsilon}^2 (A^2 - \omega^2)]. \quad (3.13)$$

Thus we can write

$$p = \frac{1}{2\alpha} \tanh \left[2\alpha \left\{ A\varepsilon - \phi \left(r e^{-A\varepsilon}, z e^{2A\varepsilon} \right) \right\} \right] - \frac{\rho}{4\mu} (r^2 - a^2) [A\ddot{\varepsilon} + \dot{\varepsilon}^2 (A^2 - \omega^2)]. \quad (3.14)$$

Substituting this value of p in (3.9) and using (3.10), we get :

$$\operatorname{sech}^2 \left[2\alpha \left\{ A\varepsilon - \phi \left(r e^{-A\varepsilon}, z e^{2A\varepsilon} \right) \right\} \right] \cdot \frac{\partial \phi}{\partial (z e^{2A\varepsilon})} e^{2A\varepsilon} + \frac{\rho}{\mu} z A (2A\dot{\varepsilon}^2 - \ddot{\varepsilon}) = 0.$$

This can be satisfied when

$$\frac{\partial \phi}{\partial (z e^{2A\varepsilon})} = 0 \quad \text{and} \quad 2A\dot{\varepsilon}^2 - \ddot{\varepsilon} = 0 \quad (3.15)$$

unless α is small which is not physically the case

Therefore we have

$$\phi = \phi \left(r e^{-A\varepsilon} \right) \text{ and } \varepsilon = (-1/2 A) \log \{ C (B + 2At) \}, \quad (3.16)$$

where C and B are arbitrary constants and can be easily determined by imposing conditions like $\varepsilon = 0$, when $t = 0$. This equation (3.16) shows that in (3.1), ε is not arbitrary.

In this way we arrive at

$$s_1^1 = s_2^2 = \frac{\rho}{4\mu} (r^2 - a^2) (3A^2 - \omega^2) (+2At + B)^{-2}, \quad (3.17)$$

$$\begin{aligned} \frac{s}{3} = \frac{3}{2\alpha} \tanh \left[2\alpha \left\{ \phi \left(r e^{-A\varepsilon} \right) - A\varepsilon \right\} \right] \\ + \frac{\rho}{4\mu} (r^2 - a^2) (3A^2 - \omega^2) (+2At + B)^{-2}, \end{aligned} \quad (3.18)$$

where $\phi(r e^{-A\varepsilon})$ can be determined from the load distribution over the plane end.

3'. REMARKS

If α is large, as generally is the case, it is obvious that the transition from elastic to plastic region is gradual and that the approach to the yield stress is quite rapid in the case of a solid cylindrical shaft rotating with constant angular velocity ω under a given load distribution at the ends.

4. PURE SHEAR UNDER LOADING (varying with time)

Referred to fixed cartesian system of coordinates, the velocity field is

$$u = c\dot{\varepsilon}x, v = -c\dot{\varepsilon}y, \omega = 0 \quad (4.1)$$

where $\dot{\varepsilon}$ is a function of t , and c is a given parameter.

The rate of deformation tensor is

$$d_{ij}^i = \begin{Bmatrix} c\dot{\varepsilon} & 0 & 0 \\ 0 & -c\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{Bmatrix} \quad (4.2)$$

We take the extra stress tensor in the form

$$t^i = \begin{Bmatrix} T & S & 0 \\ S & -T & 0 \\ 0 & 0 & 0 \end{Bmatrix}, \quad (4.3)$$

Such that $t_1^1 + t_2^2 + t_3^3 = 0$,

and S and T are functions of t only.

$$\text{Here } M = 2Tc\dot{\varepsilon} \quad (4.4)$$

Out of the equations (2.1) to (2.3) some reduce to

$$\frac{dT}{dt} = c\dot{\varepsilon} \left(1 - \frac{4}{3}\alpha^2 T^2 \right), \quad (4.5)$$

$$\frac{dS}{dt} = -\frac{4}{3}\alpha^2 T S c\dot{\varepsilon}, \quad (4.6)$$

$$\frac{\partial p}{\partial x} = -\frac{\rho}{2\mu} c \dot{x} (\ddot{\varepsilon} + c \dot{\varepsilon}^2), \quad (4.7)$$

$$\frac{\partial p}{\partial y} = -\frac{\rho}{2\mu} c \dot{y} (c \dot{\varepsilon}^2 - \ddot{\varepsilon}), \quad (4.8)$$

and others are identically satisfied.

Now on integration, the equations (4.5) and (4.6) give :

$$T = \frac{\sqrt{3}}{2\alpha} \tanh \left(\frac{2\alpha\varepsilon c}{\sqrt{3}} \right), \quad (4.9)$$

where $T = 0$ when $\varepsilon = 0$

$$\text{and } S = B \operatorname{sech} \left(\frac{2\alpha\varepsilon c}{\sqrt{3}} \right), \quad (4.10)$$

where B is a constant.

From (4.7) and (4.8) we have

$$p = -\frac{\rho c}{4\mu} [(\ddot{\varepsilon} + c \dot{\varepsilon}^2) x^2 + (c \dot{\varepsilon}^2 - \ddot{\varepsilon}) y^2]. \quad (4.11)$$

Thus the stresses are

$$S_1^1 = T + \frac{\rho c}{4\mu} [(\ddot{\varepsilon} + c \dot{\varepsilon}^2) x^2 + (c \dot{\varepsilon}^2 - \ddot{\varepsilon}) y^2], \quad (4.12)$$

$$S_2^2 = -T + \frac{\rho c}{4\mu} [(\ddot{\varepsilon} + c \dot{\varepsilon}^2) x^2 + (c \dot{\varepsilon}^2 - \ddot{\varepsilon}) y^2], \quad (4.13)$$

$$S_3^3 = \frac{\rho c}{4\mu} [(\ddot{\varepsilon} + c \dot{\varepsilon}^2) x^2 + (c \dot{\varepsilon}^2 - \ddot{\varepsilon}) y^2], \quad (4.14)$$

$$S_2^1 = S, S_3^1 = S_3^2 = 0, \quad (4.15)$$

where T and S are given by (4.9) and (4.10).

If we neglect the inertia terms, our solution becomes

$$S_1^1 = -S_2^2 = T, S_3^3 = S_3^1 = S_3^2 = S_2^1 = 0, \quad (4.16)$$

provided we choose B such that $S = 0$ when $\varepsilon = 0$

The relations (4.16) are enough to suggest, for large α , the gradual transition from elastic to plastic region and that yield stress is reached for small values of the strain in the case of Pure Shear depending on time through ε .

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SYNTHESIS OF 3, 6-DIPHENYL- Δ^4 -TETRAHYDROPHTHALIC ANHYDRIDE AND THE DYES DERIVED FROM IT - EFFECT OF INTRODUCING PHENYL GROUPS AND ALSO OF DECREASING UNSATURATION IN THE PHTHALIC ACID PORTION OF PHTHALEIN DYES

By

S. D. LOIWAL* and J. D. TEWARI

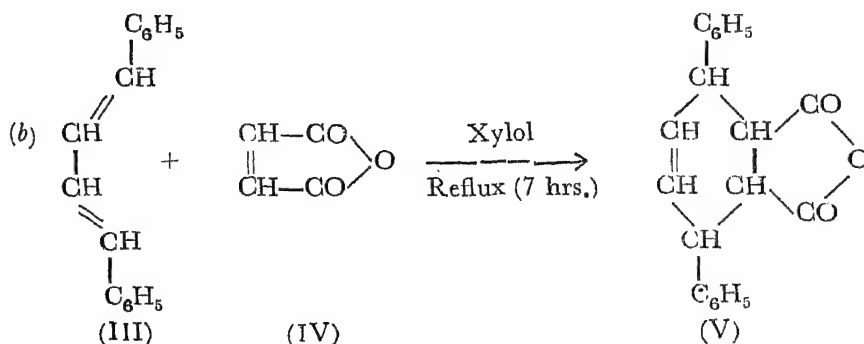
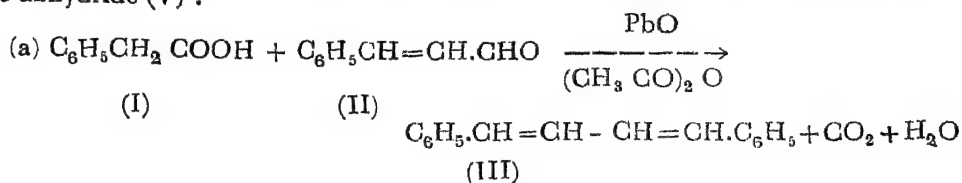
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ABSTRACT

3, 6-Diphenyl- Δ^4 -tetrahydrophthalic anhydride has been prepared and condensed with different phenols and the phthaleins obtained have been studied and compared with phthaleins from phthalic anhydride. The resorcinol phthalein has also been brominated and acetylated. The effects of introducing phenyl groups and also of decreasing unsaturation in the phthalic acid portion of phthaleins have been observed.

1, 4-Diphenylbutadiene (III) has been first prepared starting from phenyl acetic acid (I) and cinnamaldehyde (II)¹. The diene (III) has been further condensed with maleic anhydride (IV) to obtain 3, 6-diphenyl- Δ^4 -tetrahydrophthalic anhydride (V)².



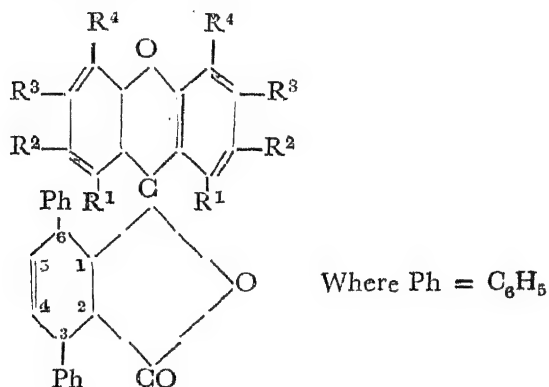
The anhydride (V) thus obtained has been condensed with resorcinol, orcinol, phenol, phloroglucinol, pyrogallol, catechol, quinol and o-cresol. The phthalein

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type of dyes obtained have been purified and analysed. The resorcinol compound has also been brominated and acetylated. Some of these dyes have been studied spectrophotometrically using British "Unicam Spectrophotometer." The absorption maxima obtained have been compared with those of phthaleins from phthalic acid.

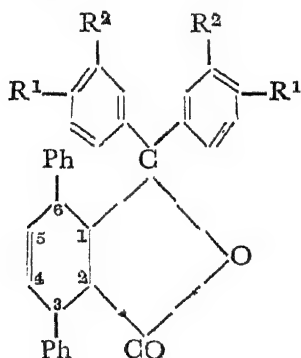
The phthaleins obtained are of the following types:

Phthaleins—Type 1



- VI: R¹=R²=R⁴=H; R³=-OH VII: R¹=-CH₃; R²=R⁴=H; R³=-OH
 VIII: R¹=R³=-OH; R²=R⁴=H. IX: R¹=R²=H; R³=R⁴=-OH
 X: R¹=R²=R³=H; R⁴=-OH. XI: R¹=R³=R⁴=H; R²=-OH
 XII: R¹=H; R²=R⁴=-Br; R³=-OH. XII: R¹=R²=R⁴=H; R³=-OCOCH₃

Phthaleins - Type 2



- XIV: R¹=-OH; R²=H XV: R¹=-OH; R²=-CH₃

EXPERIMENTAL

1, 4-Diphenyl butadiene (III) was first prepared, starting from phenyl acetic acid (I) and cinnamaldehyde (II)¹. The diene (III) after crystallisation, melted at 153°.

The diene (III) was then condensed with maleic anhydride (IV) by the method of Kuhn and Wagner-Jauregg², as follows :

1, 4-Diphenylbutadiene (10.3g) and maleic anhydride (4.6 g) were dissolved in 50 ml of xylol by warming. The mixture was refluxed for seven hours. After cooling, the colourless crystals were filtered and washed with some xylol and ethanol. The anhydride (V) thus obtained was purified by recrystallisation from chloroform. The yield of the purified 3, 6-diphenyl - Δ^4 - tetrahydrophthalic anhydride, m. p. 203°, was 11 gm. This anhydride was then used for the preparation of the corresponding phthalein type of compounds given below:

Resorcinol-3, 6-diphenyl - Δ^4 - tetrahydrophthalein (VI) - An intimate mixture of anhydride V (3 g.) and resorcinol (2.17 g) was heated for 3 hours at 180° in presence of 3-4 drops of Conc. H_2SO_4 as condensing agent. The product, after cooling was extracted with dilute NaOH and filtered. The dye was then precipitated by gradually adding dil. HCl to the alkaline filtrate. The crude dye was further purified by a second precipitation, followed by crystallisation from ethanol. It was then dried at 110° in the electric oven.

It is a red crystalline substance, m. p. 230°. The ethanolic solution is wine-red with a light green fluorescence. On adding alkali the solution turns intense wine-red with green fluorescence. (Found: C=78.5; H=4.94. $C_{32}H_{24}O_5$ requires C = 78.69; H = 4.91%).

Orcinol-3, 6-diphenyl - Δ^4 - tetrahydrophthalein (VII) - An intimate mixture of anhydride V (1 g.) and orcinol (0.82 g) was heated for five hours at 150° to 170° in presence of 2 drops of Conc. H_2SO_4 as the condensing agent. After cooling, the condensed product was powdered, extracted with dil. NaOH and filtered. The dye-stuff was precipitated from the alkaline filtrate by dil. HCl. It was further purified by crystallisation from ethanol and dried at 110° in the electric oven.

It is a brown red substance, m. p. 220°. The ethanolic solution is yellow and slightly fluorescent but on adding alkali, changes to wine-red with green fluorescence. (Found: C=78.9; H=5.45. $C_{34}H_{26}O_5$ requires C=79.07; H=5.42%).

Phloroglucinol-3, 6-diphenyl - Δ^4 - tetrahydrophthalein (VIII) - The anhydride V (1 g.) and phloroglucinol (0.83 g) were intimately mixed and heated at 180 to 190° for 3 hours in presence of 3 drops of Conc. H_2SO_4 as condensing agent. The product, after cooling, was extracted with dil. NaOH and filtered. The dye-stuff was then precipitated and purified like the resorcinol compound (VI), above.

It is a dark red crystalline substance, m. p. 245°, which dissolves in ethanol giving a yellow solution which turns blood red on adding alkali. (Found: C=73.6; H=4.65. $C_{32}H_{24}O_7$ requires C=73.84; H=4.62%).

Pyrogallol-3, 6-diphenyl - Δ^4 - tetrahydrophthalein (IX) - An intimate mixture of anhydride V (1 g.) and pyrogallol (0.83g) was heated for about five hours at 160 to 180° in presence of 3 drops of Conc. H_2SO_4 as the condensing agent. The

condensed product was crushed to a fine powder and washed with water. It was then extracted with very dil. NaOH and filtered. The dye-stuff was precipitated by adding dil. HCl to the alkaline filtrate. It was further purified by a second precipitation and crystallisation from ethanol. It was then dried at 110° in the electric oven.

It is a black powder, m. p. 240°, which dissolves in ethanol giving a brownish yellow solution which turns red brown on adding alkali. (Found: C=73·8; H=4·64. $C_{32}H_{24}O_7$ requires C=73·84; H=4·62%).

Catechol - 3, 6-diphenyl - Δ^4 -tetrahydrophthalein (X)—It was obtained from anhydride V (1 g.) and catechol (0·82 g) in the same way as the pyrogallol compound (IX) above.

It is also a black substance, m. p. 240°, which dissolves in ethanol giving a brownish yellow solution which turns red brown on adding alkali. (Found: C=78·5; H=4·93. $C_{32}H_{24}O_5$ requires C=78·69; H=4·91%).

Quinol - 3, 6-diphenyl - Δ^4 -tetrahydrophthalein (XI)—An intimate mixture of anhydride V (1 g.) and quinol (0·82 g) was condensed and the dye-stuff obtained in a similar way as the the pyrogallol compound (IX) above.

It is a black powder, m. p. 242°. The ethanolic solution is brown which turns red-brown on adding alkali. (Found: C=78·4; H=4·94. $C_{32}H_{24}O_5$ requires C=78·69; H=4·91%).

Tetrabromoresorcinol - 3, 6-diphenyl - Δ^4 -tetrahydrophthalein—(XII). It was obtained by brominating resorcinol - 3, 6-diphenyl - Δ^4 tetrahydrophthalein (VI) by the method of Baeyer³ (Preparation of eosin from fluorescein).

It is a deep red crystalline substance, m. p. 210°. The ethanolic solution is pink which changes to a red with green fluorescence on adding alkali. (Found: Br=39·47. $C_{32}H_{20}O_5Br_4$ requires Br=39·77%).

Resorcinol - 3, 6-diphenyl - Δ^4 -tetrahydrophthalein diacetate(XIII)—It was obtained by acetylating the resorcinol compound (VI) with acetic anhydride in presence of fused sodium acetate. The compound was purified by crystallisation from ethanol.

It is a brown crystalline substance, m. p. 230° (Found: C=75·3; H=4·91. $C_{36}H_{28}O_7$ requires C=75·52; H=4·89%).

Phenol - 3, 6-diphenyl - Δ^4 -tetrahydrophthalein (XIV)—A mixture of anhydride (V) (2g.) and phenol (4 g.) was heated at 110° to 115° for about 12 hours in presence of 6 drops of Conc. H_2SO_4 as condensing agent. The condensed semi-solid mass was poured into 50 ml of water and the excess of phenol was removed by steam distillation. The crude solid residue was extracted with very dil. NaOH and the phthalein precipitated by adding dil. HCl to the alkaline filtrate. The compound was further purified by decolourising the ethanolic solution with animal charcoal and then crystallising the subsequent compound with an ethanol-water mixture (2:1).

It is a dirty white substance, m. p. 160°. The ethanolic solution is slightly

yellow and turns deep pink on adding alkali. (Found : C=80.8 ; H=5.51. $C_{32}H_{26}O_4$ requires C = 81.01 ; H=5.48%).

o-Cresol - 3, 6 - diphenyl - Δ^4 - tetrahydrophthalein - (XV)—A mixture of anhydride (V) (2g.) and *o*-cresol (4g) was heated at 100° to 110° for 14 hours in presence of 6 drops of Conc. H_2SO_4 as condensing agent. The condensed semisolid mass was treated as in case of phenol compound (XIV), above, and the dye extracted, purified, and crystallised in a similar way.

It is a whitish brown substance, m. p. 143°. The ethanolic solution is light brown, which changes to a purple pink on adding alkali. (Found : C=81.1 ; H=6.0 $C_{34}H_{30}O_4$ requires C=81.27 ; H=5.97%).

The absorption maxima (λ max) of some of these compounds were determined in neutral and alkaline ethanolic solutions using British "Unicam" spectrophotometer (Table I and II)⁴. The maxima for phthaleins form phthalic anhydride were also determined using the same apparatus, under similar conditions.

TABLE I

Showing λ max of phthalein type of compounds in ethanolic solution containing a drop of 5% NaOH

Phenols	Phthaleins	3, 6 - diphenyl - Δ^4 - tetrahydrophthaleins
Resorcinol	500 m μ (fluorescein)	505 m μ
Orcinol	500 m μ (Orcein)	510 m μ
Phenol	560 m μ (Phenolphthalein)	...
Phloroglucinol	470 m μ	460 m μ
O-Cresol	570 m μ	575 m μ
Tetrabromoresorcinol	523 m μ (eosin)	540 m μ

TABLE II

Showing λ max of a few phthaleins in neutral ethanolic solution

Phenols	3, 6 - diphenyl - Δ^4 - tetrahydrophthaleins
Resorcinol	445 m μ
Orcinol	445 m μ
Tetrabromoresorcinol	530 m μ
Phloroglucinol	430 m μ

The authors express their sincere thanks to the authorities of Allahabad University, Allahabad, for providing the necessary facilities.

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ENGINEERING PROPERTIES OF SOILS: PERMEABILITY OF SOILS

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ABSTRACT

The results of water and permeability obtained on undisturbed soils indicate negative but significant correlations between water permeability and soil particles below 0.002 mm or 0.005 mm. and 0.01 mm. The density of a soil also affects its permeability. Positive significant correlations exist with D_{60} or D_{70} of soils.

Air permeability is mainly governed by its cohesion, which is better index of the hardness of soils than its dry bulk density.

The permeability of the soil for water or air is a function of the amount and size distribution of the pores. Asghar and Dhawan (2) concluded from their experiments that the permeability of a soil depended on the clay percentage, dispersion coefficient and dry bulk density.

Slichter (9) proposed a formula for the permeability of soils.

$$\text{Permeability Coefficient} = \frac{1440 \times 0.212 \times d^2}{UK_1}$$

Where d = Mean diameter of the soil grains.

U = Coefficient of viscosity of water.

K_1 = Constant which depends on the porosity of the soil.

Hazen (6) found that the permeability of sands in a loose state depended on two characteristics, that he called the effective size and the uniformity coefficient. The effective size is the diameter D_{10} , which corresponds to $P = 10\%$ on the grain size diagram. In other words 10% of the particles are finer and 90% coarser than the effective size. The uniformity coefficient U is taken as the ratio of D_{60} to D_{10} where in D_{60} is the effective grain size relating to $P = 60\%$. With the further advancement in scientific knowledge the ratio D_{70}/D_{20} was considered more significant than D_{60}/D_{10} .

A knowledge of the state at which water moves through undisturbed soils, after they have been saturated is of fundamental cum practical importance in the domain of soil engineering. Therefore an attempt was made to determine the permeability of undisturbed soil samples in order to investigate the effect of size particles and the effective size grains on the permeability of soils and to see whether some single-value soil constant was responsible for controlling the permeability.

EXPERIMENTAL

The following studies were conducted.

1. Thirty five undisturbed soil samples were taken. They were analysed for the following soil constants.

(i) Natural dry bulk density.

(ii) Mechanical analysis.

(iii) Effective grain sizes (D_{10} to D_{90}) were calculated from the summation curves drawn for each soil.

(iv) The permeability was determined under a constant head permeameter at a gradient of 1:24. It was expressed in cusecs 1 per million sq. ft. For the mechanical analysis, the soils were dispersed by the method investigated by Dhawn and his coworkers(4).

2. Fourteen undisturbed soil samples were tested for their air permeability and the comparative effect of different size particles and cohesion on air permeability was investigated. The air permeability of soil was determined by the method proposed by Kirkham (5) and the cohesion was found out by a cohesion machine (7).

DISCUSSION OF RESULTS

Diagrammatic Representation of Analytical Results.

To facilitate the comparison between the various soil characteristics, the results of analysis have been represented graphically in Figs. (I-VIII)

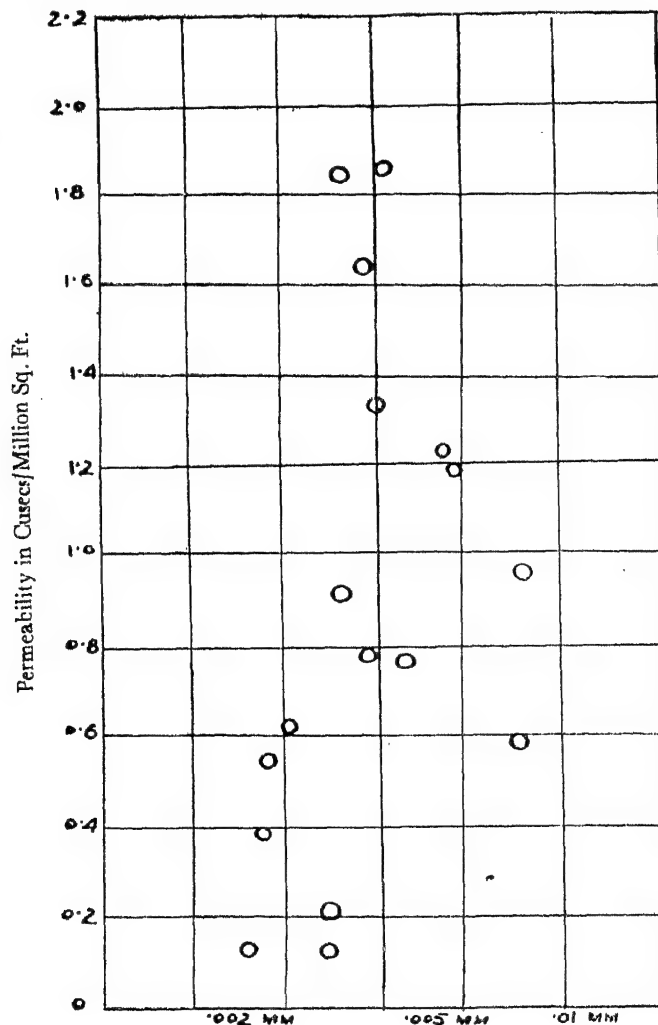


Fig. I. Relation between D 20 and Permeability of Soils.

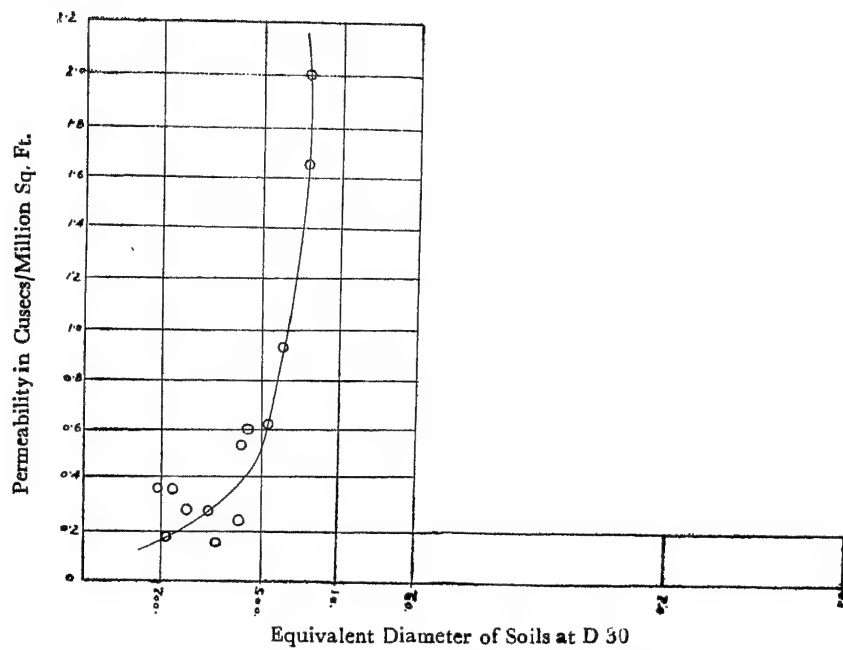


Fig. II. Relation between D 30 and Permeability of Soils.

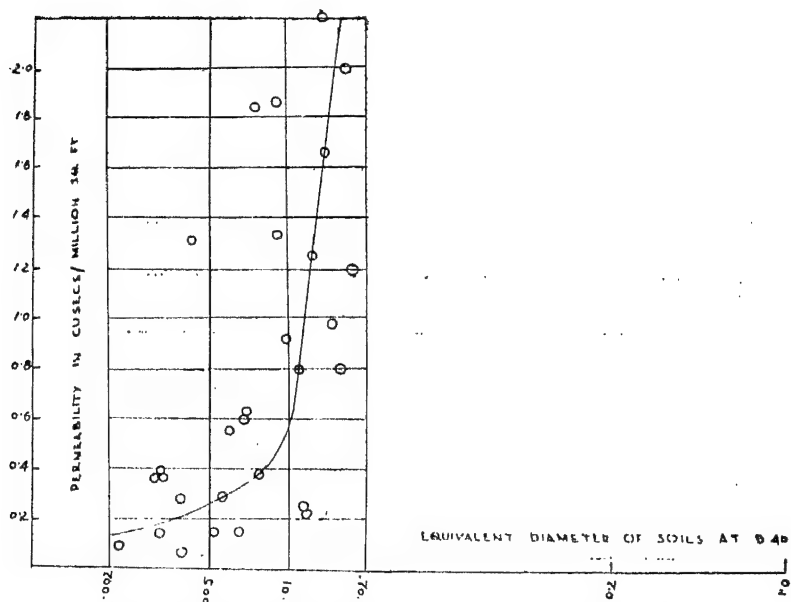


Fig. III. Relation between D 40 and Permeability of Soils.

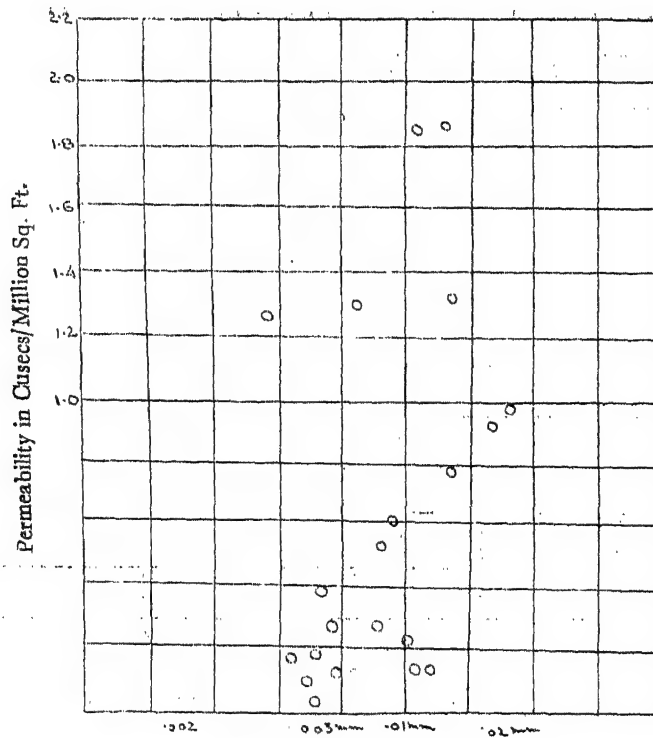


Fig. IV. Relation between D 50 and Permeability of Soils.

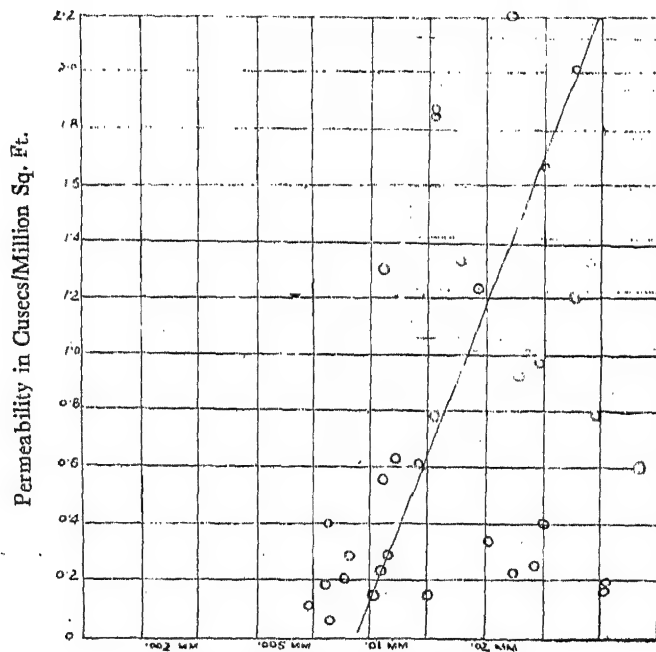


Fig. V. Relation between D 60 and Permeability of Soils.

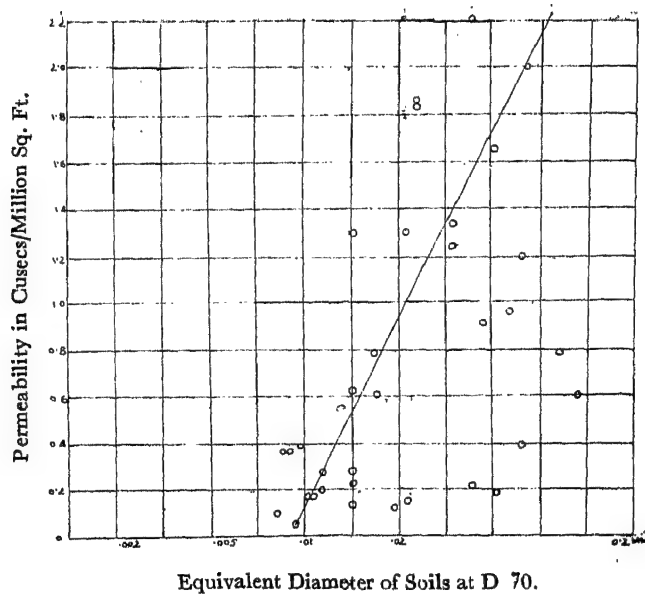


Fig. VI. Relation between D 70 and Permeability of Soils.

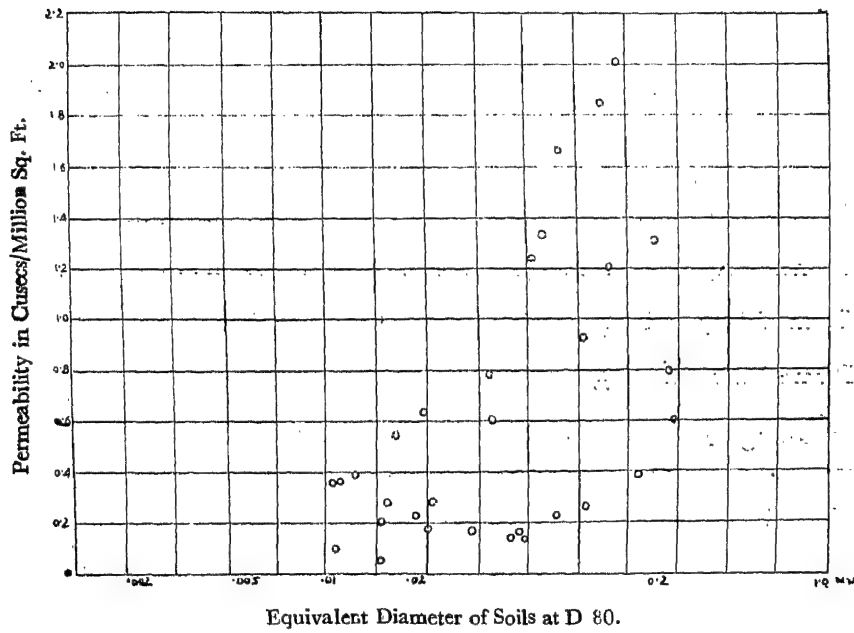


Fig. VII. Relation between D 80 and Permeability of Soils.

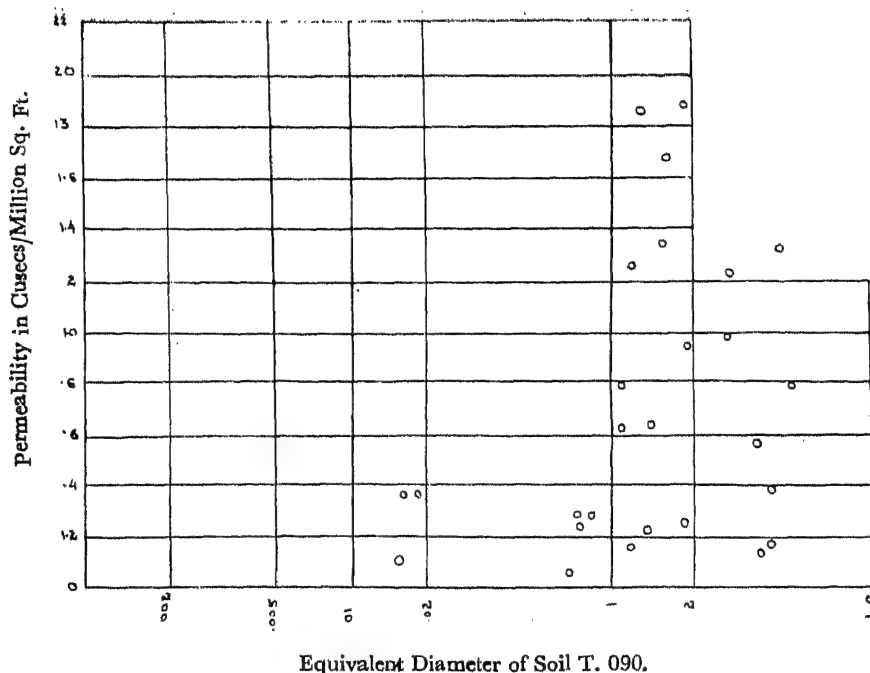


Fig. VIII. Relation between D_{90} and Permeability of Soils.

Statistical Treatment of Analytical Results.

An examination of Figs. (I-VIII) brings out diagrammatically the following relationships between the different soil constants :—

- Permeability and percentage of particles below 0.002 mm.
- Permeability and percentage of particles below 0.005 mm.
- Permeability and percentage of particles below 0.01 mm.
- Permeability and D_{60}
- Permeability and D_{70}

The following are the notations used in the statistical interpretation of analytical results.

Variable 1 = Permeability

Variable 2 = Analytical results for the characteristics under consideration
i.e. and D_{10} to D_{80}

$r_{1.2}$ = Total correlation between variables 1 and 2.

TABLE I
Correlation between Permeability and Certain Soil Characteristics

S. No.	Soil Characteristics	No. of observations	$r_{1,2}$	Remarks
1.	Particles below 0.002 mm.	35	-0.551	Significant
2.	Particles below 0.005	35	-0.5661	Significant
3.	Particles below 0.01 mm	35	-0.440	Significant
4.	Product of percentage of particles below 0.002 mm and natural dry bulk density.	35	-0.5393	Significant
5.	Product of percentage of particles below 0.005 mm and natural dry bulk density.	35	-0.6327	Significant
6.	Product of percentage of particles below 0.01 mm and natural dry bulk density.	35	-0.5604	Significant
7.	D_{60}	35	+0.4473	Significant
8.	D_{70}	35	+0.4759	Significant

The correlations of permeability with D_{10} , D_{20} , D_{30} , D_{40} , D_{50} , D_{80} , and D_{90} were insignificant.

The correlations of permeability with percentage of particles below .002 mm, below .005mm or below .01 mm are negatively significant on 1% level of significance, which shows that the high permeability is associated with low percentage of these particles. Slater and Byers (10) found a correlation between the order of permeability and the percentage of silt in the soil. These results lend support to our findings that there exists a negative significant correlation between the permeability and percentage of particles below .002 mm or .005 or 0.1 mm. All the particles lying between .002 mm and .01 mm are classified as fine silt.

It is well known that when a soil is compressed, the volume occupied by its solid constituents remains practically same, but the volume of the voids minimises. As a consequence, the permeability of the soil is bound to decrease.

The results of statistical analysis given in table I show clearly that the correlation coefficients of the product of the dry bulk density with the different size gradings are correspondingly greater than the correlation coefficients of size gradings alone with the permeability. This confirms that the dry-bulk density also affects the permeability of soils.

As pointed out in the introduction some of the workers like Hazen have pointed out the effect of the average size of the soil particles on the permeability of soils.

The correlation coefficients of the average grain size, of the soils, ranging from D_{10} to D_{90} were determined with the permeability. The results of analysis did not exhibit any relation of permeability with D_{10} to D_{50} , D_{80} and D_{90} . Significant, positive correlations were found with D_{60} and D_{70} (Table *1). A glance at the Figs. (III-X) also reveals the same fact. Though these results are contrary to Hazen's conclusions, yet they indicate that neither the very low average size grading nor very high average size grading can bear any relation with the permeability coefficient. D_{60} and D_{70} are more near about the noncapillary sizes which in otherwords confirm the findings of Baver (3) that the permeability of a soil is governed mostly by its non-capillary porosity. Permeability of soil for water is unquestionably a function of the amount of the larger pores. On the basis of the present results, it may be concluded that the average size of particles, relating to D_{60} or D_{70} may compare favourably well with the permeability coefficient.

II Air Premeability of Soils.

In table II are embodied the results of mechanical analysis, dry bulk density, cohesion, natural moisture content & air permeability measured in seconds.

TABLE II

Mechanical Analysis, Dry Bulk Density, Coesion, Natural Moisture and Air Permeability Coefficient of Undisturbed Soils

S. No.	Clay % particles below .002 mm.	Silt % particles greater than .002 mm but less than 0.02 mm.	Sand % (Particles greater than in 0.02 but less than 2.0 mm.	Dry bulk density in gms/cc	Cohesion in lbs/ sq/in.	Natural moisture	Permea- bility in seconds.
1	9.3	17.1	73.6	1.60	21	3.9	107
2	10.7	32.2	57.1	1.50	23	9.0	231
3	11.1	44.5	44.4	1.46	9	13.2	210
4	12.3	45.6	42.1	1.76	11	4.0	371
5	12.4	28.2	49.4	1.70	17	4.5	280
6	12.2	28.3	59.5	1.60	22	3.8	570
7	14.8	31.9	53.3	1.61	24	2.5	302
8	16.2	38.0	45.7	1.57	34	19.8	835
9	18.0	34.8	47.2	1.76	14	10.0	437
10	17.6	34.8	47.6	1.57	23	14.6	193
11	19.3	39.2	41.4	1.72	26	1.8	295
12	22.0	38.2	39.8	1.76	37	5.9	795
13	26.3	38.6	35.1	1.60	63	10.7	2760
14	28.2	45.2	26.6	1.59	57	10.0	2595

The results were subjected to statistical treatment. The correlations between clay, silt, sand, dry bulk density and cohesion were worked out and are given below :—

TABLE III

Correlations Between Permeability and Certain Soil Characteristics.

S. No.	Soil of Characteristics	No. of observations	r 1.2	Remarks.
1.	Clay	14	+ 0.8368	Significant on 1%
2.	Silt	14	+ 0.3732	Insignificant
3.	Sand	14	+ 0.6729	Significant on 1%
4.	Cohesion	14	+ 0.9232	—do—
5.	Dry bulk density	14	—	Insignificant.

TABLE IV

Mutual Correlation Coefficients.

S. No.	Soil Characteristics	No. of observation	Correlation coefficient	Remarks.
1.	Clay with sand	14	- 0.8100	Significant on 1%
2.	Clay with cohesion	14	+ 0.8496	—do— on 1%
3.	Clay with silt	14	+ 0.4558	—do— on 10%
4.	Silt with sand	14	- 0.9810	—do— on 1%
5.	Silt with cohesion	14	+ 0.1184	Insignificant
6.	Sand with cohesion	14	- 0.5578	Significant on 5%

As expressed, the correlations with clay and cohesion are highly significant and positive. This indicates that a high clay content will impart greater cohesion than sand, the correlation of sand with cohesion must be opposite to that of the clay.

Partial Correlation Coefficient

In view of the high significant correlations of clay, sand and cohesion on the air permeability, it was, therefore, thought necessary to determine the partial coefficient between the characteristics as it would give us an idea of the association between the two characteristics, when the effect of the third was eliminated

TABLE V
Partial Correlation Coefficients.
(Eliminating three variables)

S. No.	Soil Characteristics	Correlation coefficient	Remarks
1.	Permeability with clay when the effect of silt, sand and cohesion are deleted out	-0.00673	Insignificant
2.	Permeability with silt when the effect of clay, sand and cohesion are deleted out	-0.02422	—do—
3.	Permeability with sand when the effect of clay, silt & cohesion are deleted out	-0.011416	—do—
4.	Permeability with cohesion when the effect of clay, silt and sand are deleted out	-0.7893	Significant

The only significant correlation is with the cohesion. It is, therefore, concluded that the air permeability is mainly governed by the cohesion.

The importance of air permeability as a physical characteristic of soils was recognised by Renk (8), Wollny (II) and Ammon (1). It is generally believed that the higher the compaction, the greater is the obstruction towards air permeability. The results of the present experiments prove conclusively that the air permeability of soil is mainly dependent upon the cohesion of the soil, cohesion, in fact, determines the over all texture of a soil.

In the case of water permeability, our results pointed out that the permeability was mainly governed by the dry bulk density and percentage of particles, below .01 mm. Particles greater than .01 mm do not contribute towards cohesion. Therefore it is inferred from these results that the permeability of a soil whether for water or air is mainly related with the cohesion. Cohesion of the soil particles will undoubtedly affect the PF moisture equilibrium, which is further related with the non-capillary porosity or the water permeability of soils. In the case of air permeability, the presence of water in the soil pores restricts flow. One point of great practical importance emerges out of the above discussion. Hardness of soils is classified on the basis of their dry bulk density, which does not seem to present a true condition of the soil. A soil having low density and low moisture content can be more hard than a soil possessing greater density and greater moisture content. Therefore cohesion of a soil is a better index of the hardness of a soil.

SUMMARY

The following main conclusions were drawn :—

- (i) Negative significant correlation exists between water permeability and the following soil characteristics.
 - (a) Clay Particles below .002 mm.
 - (b) Particles below .005.
 - (c) Particles below .01 mm (Clay plus fine silt).
 - (d) Product of clay and dry bulk density.
 - (e) Product of percentage of particles below .005 mm and dry bulk density.
 - (f) Product of percentage of particles below .01 mm and dry bulk density.
- (ii) Positive significant correlations are investigated between water permeability and D_{80} or D_{70} of soils.
- (iii) There is no significant correlation of water permeability with D_{10} to D_{50} or D_{80} and D_{90} of soils.
- (iv) Air permeability in soil is mainly governed by its cohesion.
- (v) Cohesion is a better index of the hardness of soil than dry bulk density.

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RADIAL OSCILLATIONS OF VARIABLE MAGNETIC STAR AND THE ORIGIN OF THE PLANETARY SYSTEM

By

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ABSTRACT

A variable magnetic star of spherical shape having mass nine times that of the sun was supposed to oscillate initially with small amplitude. It has been shown that the nearby passage of a star of about the same mass increased the amplitude of the oscillations of the magnetic star rendering them unstable. Consequently matter was thrown out from the magnetic star, and from this matter the sun and the planets might possibly have been formed. It is assumed that the magnetic lines of force lie on spherical surfaces concentric with the star and the electric currents also flow along these surfaces. The mechanical force of electromagnetic origin will be perpendicular to the magnetic field. The magnetic field H can be expressed in spherical coordinates. A simple possible form of H has been assumed. It is not necessary that the encounter should be close nor it is necessary that the intruding star should have an inordinately large velocity in order that the sun and the planets might have requisite angular velocity and might take sufficient energy from the parent magnetic star to escape from it. The sun with its planetary system need only take part of the magnetic energy of the parent star.

The earlier theory of Banerji¹ on the instability of radial oscillations of a variable star and the origin of the planetary system suggests that a star by approaching a pulsating cepheid variable star has caused it to throw matter which resulted in a planetary system. The theory was deduced solely from hydrodynamical considerations. It is well known that the magnetic field of the order of one gauss exists on the surface of the sun. General magnetic fields of the order of a few thousand gauss have also been observed in the reversing layers of some stars. The observed polarisation in the light of distant stars seem to suggest the existence of a magnetic field of the order of 10^{-6} gauss in them. It is quite evident that these accompanying magnetic fields will play an important part in the dynamics of the solar system. From theoretical considerations it is sometimes believed that all stars may have strong fields somewhere in their interior or in their atmospheres. But the reasons for this belief are not decisive. It may be regarded as a possibility or conjecture. A number of investigators have imposed magnetic fields of arbitrary geometry² on spherical stars. An axisymmetric form of a magnetic field which is strictly compatible with spherical boundaries has been found by Prendergash,³ Chandra Shekhar⁴ and Fermi⁴ have shown that a uniform magnetic field tends to produce an oblate spheroid by contracting the sphere along the direction of the field.

In our case we have assumed that the magnetic star has a spherical shape and is subject to small radial oscillations. It is assumed that the magnetic lines of force lie on spherical surfaces concentric with the star and the electric currents also flow along those surfaces. The mechanical force of electromagnetic origin will be perpendicular to the magnetic field. We shall consider here the radial motion. H can be expressed in terms of spherical coordinates.⁵ We assume a

simple possible form for H which may be taken as $\frac{l_1 S_q}{r^{q+2}}$, where, q is a positive

integer, l_1 is a constant and S_q is a surface harmonic of order q .

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Let H_0 be the undisturbed value corresponding to H at a point. For a steady flow H_0 does not vary with time.

We shall investigate the small adiabatic oscillations of a magnetic star. In our investigations we shall retain the square of the amplitude.

Let P and ρ be the pressure and density at a point distant ξ from the centre and let g be the value of gravity there. Let ξ_0 , P_0 , ρ_0 and g_0 denote the undisturbed values. We fix our attention on a particular piece of matter at distance ξ from the centre so that ξ oscillates with pulsations.

Eddington (1926) and Sterne (1937) considered only very small radial oscillations the squares of whose amplitude could be neglected. But we shall retain the square of the amplitude in our equations and try to investigate their solutions.

We are concerned with the motion of a particular piece of matter⁶, and hence we write down the equation of motion of a particle along the radius vector,

$$\ddot{\xi} - \xi \dot{\theta}^2 = R - \frac{1}{\rho} \frac{dP}{d\xi} \quad (1)$$

where, R is the component of external forces per unit mass in the direction of ξ . Viscosity is neglected.

The star is supposed to have only small radial oscillations and it is assumed to have a spherical form so that if any transverse velocity is generated due to H , it is very small and negligible. In another paper we shall investigate the oscillations of an oblate rotating spheroid and take account of the transverse motion. Strictly speaking, due to H , the displacement of an element of matter initially at ξ_0 , θ_0 is not merely a function of ξ_0 and the time but depends upon θ_0 also. There will thus be greater degree of damping⁷ than what is associated with the spherically symmetrical type of oscillations. It does not concern us to find out the exact measure of the displacement. We are required merely to investigate the stability or otherwise of the radial oscillation.

Neglecting $\dot{\theta}$ in the present case, the equation reduces to

$$\ddot{\xi} = R - \frac{1}{\rho} \frac{dP}{d\xi} \quad (2)$$

The second equation is a statical equation.

Now $R = -\frac{g_0 \xi_0^2}{\xi^2} + (\bar{J} \times \mu \bar{H})_{\xi}$ where $(\bar{J} \times \mu \bar{H})_{\xi}$ is the component of $(\bar{J} \times \mu \bar{H})$ in the direction of ξ . (3)

Here J is the electric current density and μ is permeability

$$\text{Now}^8 (\bar{J} \times \mu \bar{H}) = -\text{grad} \left(\frac{\mu H^2}{8\pi} \right) + \text{div} \left(\frac{\mu H \bar{H}}{4\pi} \right) \quad (4)$$

where the last term denotes the divergence of a dyad. This equation implies that

the force $(\vec{J} \times \mu \vec{H})$ is equivalent to a hydrostatic pressure $\frac{\mu H^2}{8\pi}$ together with a tension $\frac{\mu H^2}{4\pi}$ along the lines of force.

We therefore get the radial equation, neglecting viscosity

$$\ddot{\xi} = -\frac{g_0 \xi_0^2}{\xi^3} - \frac{1}{\rho} \frac{d}{d\xi} \left(P + \frac{\mu H^2}{8\pi} \right) \quad (5)$$

where ξ, g, ρ and P denote distance from centre, gravity, density and pressure respectively, at a point, and ξ_0, g_0, ρ_0 and P_0 are the corresponding values at the same point in the undisturbed state of the star. \vec{H} is the strength of the magnetic field given by

$$H = \frac{l_1 S_q}{\xi^{q+2}} = \frac{l}{\xi^{q+2}} \quad (6)$$

we take $l_1 S_q = l$, because we have to consider the radial oscillations in a fixed direction θ, ϕ

Define ξ_1, ρ_1, P_1 and H_1 by

$$\xi = \xi_0 (1 + \xi_1), \rho = \rho_0 (1 + \rho_1), P = P_0 (1 + P_1), H = H_0 (1 + H_1) \quad (7)$$

where ξ_1, ρ_1, P_1 and H_1 are small quantities.

We shall keep later on small quantities of the second order, that is, upto ξ_1^2 etc.

During the motion the following equation remains true :

$$\rho_0 \xi_0^3 d\xi_0 = \rho \xi^2 d\xi \quad (8)$$

For adiabatic changes the pressure and density of a particular piece of matter are connected by the relation

$$P = k\rho^\gamma \quad (9)$$

where γ is the effective ratio of specific heats (regarding the matter and enclosed radiation as one system).

We get from (7), (8), (9)

$$1 + \rho_1 = \frac{1}{(1 + \xi_1)^2 (1 + \xi_1 + \xi_0 \xi_1')} \quad (10)$$

$$1 + P_1 = \frac{1}{(1 + \xi_1)^{2\gamma} (1 + \xi_1 + \xi_0 \xi_1')^\gamma} \quad (11)$$

$$1 + H_1 = \frac{H}{H_0} = \frac{1}{(1 + \xi_1)^{q+2}} \quad (12)$$

where $\xi_1' = \frac{d\xi_1}{d\xi_0}$ (13)

we therefore have

$$\ddot{\xi} = - \frac{g_0}{(1+\xi_1)^2} - \frac{(1+\xi_1)^2}{\rho_0} \left\{ (1+P_1) \frac{dP_0}{d\xi_0} + P_0 \frac{d\rho_1}{d\xi_0} \right\} - \frac{(1+\xi_1)^2}{\rho_0} - \frac{\mu}{8\pi} \frac{dH^2}{d\xi_0} \quad (14)$$

From equation of undisturbed state we get

$$\begin{aligned} \frac{dP_0}{d\xi_0} &= -g_0 \rho_0 \\ \text{and } \frac{dH^2}{d\xi_0} &= \frac{d}{d\xi_0} \{ H_0^2 (1+H_1)^2 \} = (1+H_1)^2 2H_0 \frac{dH_0}{d\xi_0} + 2H_0^2 (1+H_1) \frac{dH_1}{d\xi_0} \\ &= - \frac{2l^2(q+2)(1+\xi_1+\xi_0\xi_1')}{\xi_0^{2q+5}(1+\xi_1)^{2q+5}} \end{aligned} \quad (15)$$

where $H_0 = \frac{l}{\xi_0^{q+2}}$

The equation (14) may now be put into the form

$$\begin{aligned} \ddot{\xi} &= -\xi_0 \left[\frac{1}{(1+\xi_1)^2} - \frac{1}{(1+\xi_1)^2 \gamma^{-2} (1+\xi_1+\xi_0\xi_1')^\gamma} \right] - \frac{P_0 (1+\xi_1)^2}{\rho_0} \frac{d}{d\xi_0} \\ &\quad \left[\frac{1}{(1+\xi_1)^2 \gamma (1+\xi_1+\xi_0\xi_1')^\gamma} \right] + \frac{\mu (1+\xi_1)^2}{8\pi \rho_0} \left[\frac{2l^2(q+2)(1+\xi_1+\xi_0\xi_1')}{\xi_0^{2q+5}(1+\xi_1)^{2q+5}} \right] \end{aligned} \quad (16)$$

Approximations⁹

We shall neglect higher powers of ξ_1 etc. than the second

$$\begin{aligned} (1+\rho_1) &= 1 - \gamma(3\xi_1 + \xi_0\xi_1') + \left\{ \frac{\gamma(\gamma+1)}{2} \xi_0^2 \xi_1'^2 + \frac{3}{2} \gamma(3\gamma+1) \xi_1'^2 + \gamma(3\gamma+1) \xi_0 \xi_1 \xi_1'' \right\} \\ \frac{dP_1}{d\xi_0} &= -\gamma(4\xi_1' + \xi_0\xi_1'') + \left[\gamma(4\gamma+2) \xi_0 \xi_1'^2 + \gamma(\gamma+1) \xi_0^2 \xi_1' \xi_1'' + 4\gamma(3\gamma+1) \xi_1 \xi_1' + \right. \\ &\quad \left. \gamma(3\gamma+1) \xi_1 \xi_1'' \xi_0 \right], \quad \text{where } \frac{d^2 \xi_1}{d\xi_0^2} = \xi_1'' \end{aligned}$$

Hence $(1+P_1)(1+\xi_1)^2 = 1 - \left\{ (3\gamma-2) \xi_1 + \gamma \xi_0 \xi_1' \right\} + \left\{ \left(\frac{9}{2} \gamma^2 - \frac{9}{2} \gamma + 1 \right) \xi_1^2 + \right.$

$$\left. \gamma(3\gamma-1) \xi_0 \xi_1 \xi_1' + \frac{\gamma(\gamma+1)}{2} \xi_0^2 \xi_1'^2 \right\}.$$

$$(1+\xi_1)^2 \cdot \frac{dP_1}{d\xi_0} = -\gamma(4\xi_1' + \xi_0\xi_1'') + \left\{ 4\gamma(3\gamma-1) \xi_1\xi_1'' + 2\gamma(2\gamma+1) \xi_0\xi_1'^2 + \right. \\ \left. \gamma(3\gamma-1) \xi_0\xi_1\xi_1'' + \gamma(\gamma+1) \xi_0^2 \xi_1' \xi_1'' \right\} \\ (1+\xi_1)^{-(2q+3)} = \left\{ 1 - (2q+3) \xi_1 + (2q+3)(q+2) \xi_1^2 \right\}$$

$$(H\xi_1)^{-(2q+3)} (1+\xi_1+\xi_0\xi_1') \\ = \left[1 - (2q+2) \xi_1 + (2q+3)(q+1) \xi_1^2 + \xi_0\xi_1' - (2q+3) \xi_0\xi_1\xi_1' \right]$$

We, therefore, get from equations (14) and (15)

$$\ddot{\xi} = g_0 \left[\left\{ - (3\gamma-4) \xi_1 - \gamma\xi_0\xi_1' \right\} + \left\{ \left(\frac{9}{2} \gamma^2 - \frac{9}{2} \gamma - 2 \right) \xi_1^2 + \gamma(3\gamma-1) \right. \right. \\ \left. \left. \xi_0\xi_1\xi_1' + \frac{\gamma(\gamma+1)}{2} \xi_0^2 \xi_1'^2 \right\} \right] + \frac{P_0}{\rho_0} \gamma \left[(4\xi_1' + \xi_0\xi_1'') - \left\{ 4(3\gamma-1) \xi_1\xi_1' + \right. \right. \\ \left. \left. 2(2\gamma+1) \xi_0\xi_1'^2 + (3\gamma-1) \xi_0\xi_1\xi_1'' + (\gamma+1) \xi_0^2 \xi_1'^2 \xi_1'' \right\} \right] + \\ \frac{S}{\xi_0^{2q+5}} \left[1 - (2q+2) \xi_1 + (2q+3)(q+1) \xi_1^2 + \xi_0\xi_1' - (2q+3) \xi_0\xi_1\xi_1' \right] \quad (17)$$

$$\text{where } S = \frac{\mu l^2(q+2)}{4\pi \rho_0}$$

Let us assume in the beginning that ξ_1 is small and that

$$\xi_1 = a_1(\xi_0) \cos nt - a_2(\xi_0) \cos 2nt - a_3(\xi_0) \quad (18)$$

where $a_1(\xi_0)$ is a small quantity of the first order and $a_2(\xi_0)$ and $a_3(\xi_0)$ are small quantities of the second order in ξ_1 we neglect small quantities of the second and higher orders.

$$\text{Now } \xi = \xi_0 (1 + \xi_1), \quad \text{where } \dot{\xi} = \frac{d\xi}{dt}, \quad \ddot{\xi} = \frac{d^2\xi}{dt^2}$$

$$\text{Hence } \ddot{\xi} = \xi_0 \ddot{\xi}_1 = -n^2 \xi_0 \left\{ a_1(\xi_0) \cos nt - 4a_2(\xi_0) \cos 2nt \right\} \quad (19)$$

$$\xi_1' = a_1'(\xi_0) \cos nt - a_2'(\xi_0) \cos 2nt - a_3'(\xi_0) \quad (20)$$

$$\xi_1'' = a_1''(\xi_0) \cos nt - a_2''(\xi_0) \cos 2nt - a_3''(\xi_0) \quad (21)$$

$$\text{where } \xi_1' = \frac{d\xi_1}{d\xi_0}, \quad \xi_1'' = \frac{d^2\xi_1}{d\xi_0^2}, \text{ etc.}$$

substituting in (17) we have

$$\begin{aligned}
 & \left[n^2 a_1 \xi_0 + g_0 \left\{ - (3\gamma - 4) a_1 - \gamma \xi_0 a_1' \right\} + \frac{P_0 \gamma}{\rho_0} \left\{ 4 a_1' + \xi_0 a_1'' \right\} + \frac{S}{\xi_0^{2q+5}} + \right. \\
 & \left. \left\{ \xi_0 a_1' - 2(q+1) a_1 \right\} \right] \cos nt + \left[- 4 n^2 \xi_0 a_2 + g_0 \left\{ (3\gamma - 4) a_2 + \gamma \xi_0 a_2' + \frac{1}{4} \right. \right. \\
 & (3\gamma - 4) (3\gamma + 1) a_1^2 + \frac{1}{2} \gamma (3\gamma - 1) \xi_0 a_1 a_1' + \frac{1}{4} (\gamma + 1) \gamma \xi_0 a_1'^2 \left. \right\} + \frac{P_0 \gamma}{\rho_0} \left\{ - 4 a_2' \right. \\
 & - \xi_0 a_2'' - 2 (3\gamma - 1) a_1 a_1' - (2\gamma + 1) \xi_0 a_1'^2 - \frac{1}{2} (3\gamma - 1) \xi_0 a_1 a_1'' - \frac{1}{2} (\gamma + 1) \\
 & \left. \xi_0^2 a_1' a_1'' \right\} + \frac{S}{\xi_0^{2q+5}} \left\{ 2 (q+1) a_2 + \frac{1}{2} (q+1) (2q+3) a_1^2 - \xi_0 a_2' - \frac{(2q+3)}{2} \right. \\
 & \left. \xi_0 a_1 a_1' \right\} \left. \right] \cos 2nt + \left[g_0 \left\{ (3\gamma - 4) a_3 + \gamma \xi_0 a_3' + \frac{1}{4} (3\gamma - 4) (3\gamma + 1) a_1^2 + \right. \right. \\
 & \left. \frac{1}{2} \gamma (3\gamma - 1) \xi_0 a_1 a_1' + \frac{1}{4} \gamma (\gamma + 1) \xi_0^2 a_1'^2 \right\} + \frac{P_0 \gamma}{\rho_0} \left\{ - 4 a_3' - \xi_0 a_3'' - 2 (3\gamma - 1) a_1 a_1' \right. \\
 & - (2\gamma + 1) \xi_0 a_1'^2 - \frac{1}{2} (3\gamma - 1) \xi_0 a_1 a_1'' - \frac{1}{2} (\gamma + 1) \xi_0^2 a_1' a_1'' \left. \right\} + \frac{S}{\xi_0^{2q+5}} \\
 & \left. \left\{ 1 + 2 (q+1) a_3 + \frac{1}{2} (q+1) (2q+3) a_1^2 - \xi_0 a_3' - \frac{(2q+3)}{2} \xi_0 a_1 a_1' \right\} \right] = 0 \quad (22)
 \end{aligned}$$

Putting the coefficients of $\cos nt$, $\cos 2nt$, and the terms independent of time to be separately zero, we get,

$$a_1'' + \left[\frac{4-\nu}{\xi_0} + \frac{S}{\xi_0^{2q+4}} \right] a_1' + \left[\frac{n^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} - \frac{2(q+1)S}{\xi_0^{2q+5}} \right] a_1 = 0 \quad (23)$$

$$a_2'' + \left[\frac{4-\nu}{\xi_0} - \frac{S}{\xi_0^{2q+4}} \right] a_2' + \left[\frac{4n^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} + \frac{2(q+1)S}{\xi_0^{2q+5}} \right] a_2 = Q \quad (24)$$

$$a_3'' + \left[\frac{4-\nu}{\xi_0} - \frac{S}{\xi_0^{2q+4}} \right] a_3' + \left[- \frac{\alpha \nu}{\xi_0^2} - \frac{2(q+1)S}{\xi_0^{2q+5}} \right] a_3 = Q \quad (25)$$

$$\text{where } \nu = \frac{g_0 \rho_0 \xi_0}{P_0}, \quad \alpha = 3 - \frac{4}{\gamma} \quad \text{and} \quad S = \frac{\mu(q+2)l^2}{4\pi \rho_0} \quad (26)$$

$$\text{and } Q = \left\{ \frac{1}{2} (3\gamma - 1) \frac{n^2 \rho_o}{\rho_o \gamma} - \frac{3}{4} (\gamma - 1) \frac{a \nu}{\xi_o^2} - \frac{S}{\xi_o^{2q+5}} \frac{(q+1)(2q+3)}{2} \right\} a_1^2$$

$$+ \xi_o a_1 a_1' \left[\frac{2q+3}{2} \frac{S}{\xi_o^{2q+5}} + \frac{1}{2} (\gamma + 1) \left\{ \frac{n^2 \rho_o}{\rho_o \gamma} - \frac{a \nu}{\xi_o^2} \right\} \right]$$

$$+ \left\{ 1 - \frac{1}{4} (\gamma + 1) \nu \right\} a_1'^2 \quad (27)$$

Boundary Conditions :—

From equation (6), we get

$$\frac{(1+\xi_1)^2}{\rho_o} \frac{d}{d\xi_o} (P_o P_1) + \ddot{\xi} = g_o \left\{ (1+\xi_1)^2 - \frac{1}{(1+\xi_1)^2} \right\} - \frac{(1+\xi_1)^2}{\rho_o} \frac{\mu}{8\pi} \frac{dH^2}{d\xi_o} \quad (28)$$

$$\text{and } \frac{1}{\rho_o} \frac{dP_o}{d\xi_o} = -g_o$$

we get,

$$-(1+\xi_1)^2 \frac{d}{dP_o} (\rho_o P_1) + \ddot{\xi}/g_o = \left\{ (1+\xi_1)^2 - \frac{1}{(1+\xi_1)^2} \right\} + \frac{S}{g_o \xi_o^{2q+5}}$$

$$\left\{ 1 - 2(q+1)\xi_1 + (2q+3)(q+1)\xi_1^2 + \xi_o \xi_1' - (2q+3)\xi_o \xi_1 \xi_1' \right\} \quad (29)$$

At the boundary P_o is infinitely small, and

$$\frac{d(P_o P_1)}{dP_o} = P_1$$

Hence at the boundary

$$-(1+\xi_1)^2 P_1 + \ddot{\xi}/g_o = \left\{ (1+\xi_1)^2 - \frac{1}{(1+\xi_1)^2} \right\} + \frac{S}{g_o R^{2q+5}} \left\{ 1 - 2(q+1)\xi_1 + \right.$$

$$\left. (2q+3)(q+1)\xi_1^2 + R\xi_1' - (2q+3)R\xi_1 \xi_1' \right\} \quad (30)$$

where $\xi_1, g_o, \ddot{\xi}$ have their corresponding values at the boundary and $\xi_o = R$.

Now (30) may be put in the form

$$(1+P_1) (1+\xi_1)^2 = \ddot{\xi}/g_o + \frac{1}{(1+\xi_1)^2} - \frac{S}{\xi_o^{2q+5}} \left\{ 1 - 2(q+1)\xi_1 + (2q+3)(q+1)\xi_1^2 + \right.$$

$$\left. R\xi_1' - (2q+3)R\xi_1 \xi_1' \right\} \quad (31)$$

Now, we have, upto small quantities of the second order,

$$P_1 = \gamma(3\xi_1 + R\xi_1') + \left\{ \frac{1}{2} \gamma (\gamma+1) R^2 \xi_1'^2 + \gamma (3\gamma+1) R \xi_1 \xi_1' + \frac{3}{2} \gamma (3\gamma+1) R \xi_1 \xi_1' + \frac{3}{2} \gamma (3\gamma+1) \xi_1^2 \right\}$$

Now, substituting in (31), we get at the boundary

$$\ddot{\xi}/g = - \left\{ (3\gamma-4) \xi_1 + \gamma \xi_1' R \right\} + \left\{ \frac{1}{2} (3\gamma-4) (3\gamma+1) \xi_1^2 + \gamma(3\gamma-1) R \xi_1 \xi_1' + \frac{1}{2} \gamma (\gamma+1) R^2 \xi_1'^2 \right\} + \frac{S}{g_o R^{2q+5}} \left\{ 1 - 2(q+1) \xi_1 + (2q+3) (q+1) \xi_1^2 + R \xi_1' - (2q+3) \xi_1 \xi_1' \right\} \quad (32)$$

At the boundary $\xi_o = R$.

Now putting $N = \frac{S}{g_o R^{2q+5}}$, (32) reduces to

$$\ddot{\xi}/g = N - \left[\left\{ (3\gamma-4) - N (2q+2) \right\} \xi_1 + R \xi_1' (\gamma-N) \right] + \left[\left\{ \frac{1}{2} (3\gamma-4) (3\gamma+1) + N (2q+3) (q+1) \right\} \xi_1^2 + \left\{ \gamma (3\gamma-1) - N (2q+3) \right\} R \xi_1 \xi_1' + \frac{1}{2} \gamma (\gamma+1) R^2 \xi_1'^2 \right] \quad (32A)$$

Now substituting for ξ_1, ξ_1' and $\ddot{\xi}$ from (18), (19) and (20) and equating the coefficient of $\cos nt$, $\cos 2nt$ and the term independent of them separately to zero, we get at $\xi_o = R$.

$$a_1' \left(1 - \frac{N}{\gamma} \right) + a_1 \left\{ \frac{\alpha}{R} - \frac{n^2}{g_o \gamma} - \frac{2N(q+1)}{R\gamma} \right\} = 0 \quad (33)$$

$$a_2' \left(1 - \frac{N}{\gamma} \right) + a_2 \left\{ \frac{\alpha}{R} - \frac{2N}{R\gamma} (q+1) - \frac{4n^2}{g_o \gamma} \right\} + \frac{1}{2} \left\{ \frac{\alpha}{2R} (3\gamma+1) + \frac{N(2q+3)(q+1)}{R\gamma} \right\} a_1^2 + \frac{1}{2} \left\{ (3\gamma-1) - \frac{N}{\gamma} (2q+3) \right\} a_1 a_1' + \frac{1}{4} (\gamma+1) R a_1'^2 = 0 \quad (34)$$

$$a_3' \left(1 - \frac{N}{\gamma} \right) + a_3 \left\{ \frac{\alpha}{R} - \frac{2N}{R\gamma} (q+1) \right\} + \frac{1}{2} \left\{ \frac{\alpha}{2R} (3\gamma+1) + \right.$$

$$\left\{ \frac{N(2q+3)(q+1)}{R\gamma} \right\} a_1^2 + \frac{1}{2} \left\{ (3\gamma-1) - N(2q+3) \right\} a_1 a_1' + \frac{1}{4} (\gamma+1) R a_1'^2 = 0 \quad (35)$$

Case I Sphere of uniform density.

We consider a sphere of undisturbed uniform density ρ .

The mass of the sphere of radius $\xi_0 = \frac{4}{3} \pi \bar{\rho} \xi_0^3$; the undisturbed value of gravity and pressure are :—

$$g_0 = \frac{4}{3} \pi G \bar{\rho} \xi_0 \quad \text{and} \quad P_0 = \frac{2\pi}{3} G \bar{\rho}^2 (R^2 - \xi_0^2) \quad (36)$$

Where G is the constant of gravitation and R , the radius of the undisturbed star. we have from (26) and (36)

$$\nu = \frac{2x^2}{1-x^2}, \quad \text{where } \xi_0 = Rx$$

substituting the value of g_0 , P_0 and ν and putting $\xi_0 = Rx$ in (23), (24) and (25), we get

$$x^{2q+5} (1-x^2) \frac{d^2 a_1}{dx^2} + \left[(4-6x^2) x^{2q+4} + Lx(1-x^2) \right] \frac{da_1}{dx} + \left[(\beta-2\alpha) x^{2q+5} - 2(q+1)(1-x^2)L \right] a_1 = 0 \quad (37)$$

$$x^{2q+5} (1-x^2) \frac{d^2 a_2}{dx^2} + \left[(4-6x^2) x^{2q+4} - Lx(1-x^2) \right] \frac{da_2}{dx} + \left[(4\beta-2\alpha) x^{2q+5} + 2(q+1)(1-x^2)L \right] a_2 = Q_0 \quad (38)$$

$$\text{and } x^{2q+5} (1-x^2) \frac{d^2 a_3}{dx^2} + \left[(4-6x^2) x^{2q+4} - Lx(1-x^2) \right] \frac{da_3}{dx} + \left[-2\alpha x^{2q+5} - 2(q+1)(1-x^2)L \right] a_3 = Q_0 \quad (39)$$

where $L = S/R^{4q+3}$

$$\text{and } Q_0 = \left\{ \frac{1}{2} (3\gamma-1) \beta - \frac{3}{2} (\gamma-1) \alpha + (q+1)(2q+5) \frac{L}{2R^2 x^{2q+5}} \right\} a_1^2 + \left\{ \frac{x}{2} (\gamma+1) (\beta-2\alpha) + \frac{(2q+3)L}{R^2 x^{2q+4}} \right\} a_1 \frac{da_1}{dx} + \left\{ 1 - \frac{1}{2} (\gamma+3) x^2 \right\} \left(\frac{da_1}{dx} \right)^2 \quad (40)$$

$$\text{and } \beta = \frac{3n^2}{2\pi G \rho \gamma}$$

We now put dashes for differentiation with respect to x . The boundary conditions are at $x=1$

$$2a_1' + (2\alpha - \beta) a_1 = 0 \quad (41)$$

$$2a_2' + (2\alpha - 4\beta) a_2 + \left\{ \frac{1}{2} \alpha (3\gamma + 1) - \frac{1}{2} (q+1) (2q+3) \frac{L}{R^2} \right\} a_1^2 + \left\{ (3\gamma - 1) + \frac{1}{2} (2q+3) \frac{L}{R^2} \right\} a_1 a_1' + \frac{1}{2} (\gamma + 1) a_1'^2 = 0 \quad (42)$$

$$\text{and } 2a_3' + 2\alpha a_3 + \left\{ \frac{1}{2} \alpha (3\gamma + 1) - \frac{1}{2} (q+1) (2q+3) \frac{L}{R^2} \right\} a_1^2 + \left\{ (3\gamma - 1) + \frac{1}{2} (2q+3) \frac{L}{R^2} \right\} a_1 a_1' + \frac{1}{2} (\gamma + 1) a_1'^2 = 0 \quad (43)$$

where a_1, a_1' have their relevant values at $x = 1$

We shall now get the solution in series of the equation (37) and investigate the convergence of the series in the interval $0 \leq x \leq 1$.

It is evident from the form of (37) that the boundary condition (33) will be satisfied if a_1'' remains finite at $x = 1$.

The differential equation (37) is of the second order and it has irregular singularity of the order of $(2q+5)$ at the origin and a regular singularity at $x = 1$.

Substituting in the differential equation (37) the following

$$\text{series } a_1 = x^c \sum_{\lambda=0}^{\infty} b_{\lambda} x^{\lambda} \quad (44)$$

By equating the coefficient of the lowest power of x , we get the indicial equation which gives only one root.

$$c = 2(q+1) \quad (45)$$

We, therefore, expand the solution about the origin in a power series of the form (44) where c is given by (45), and assume arbitrarily $b_0 = 1$, (as the equation is linear).

We obtain a 4 term recurrence formula.

$$b_{\lambda} \left[(2q+\lambda+2) (2q+\lambda+5) \right] - b_{\lambda-2} \left[(2q+\lambda) (2q+\lambda+5) + (\beta - 2\alpha) \right] + \\ + L b_{2q+\lambda+3} (2q+\lambda+3) - L b_{2q+\lambda+1} (2q+\lambda+1) = 0 \quad (46)$$

Arranging in powers of λ and dividing by $b_{\lambda-2}$, we get

$$\begin{aligned} \lambda^2 \left\{ \frac{b_{\lambda}}{b_{\lambda-2}} - 1 \right\} + \lambda \left[\left\{ \frac{b_{\lambda}}{b_{\lambda-2}} (4q+7) - (4q+5) \right\} + L \left\{ \frac{b_{2q+\lambda+3}}{b_{\lambda-2}} \right. \right. \\ \left. \left. - \frac{b_{2q+\lambda+1}}{b_{\lambda-2}} \right\} \right] + \left[(2q+2)(2q+5) \frac{b_{\lambda}}{b_{\lambda-2}} - \left\{ 2q(2q+5) + (\beta-2\alpha) \right\} \right. \\ \left. + L \left\{ \frac{b_{2q+\lambda+3}}{b_{\lambda-2}} (2q+3) - \frac{b_{2q+\lambda+1}}{b_{\lambda-2}} (2q+1) \right\} \right] = 0 \end{aligned} \quad (47)$$

Dividing by λ^2 and proceeding to the limit as $\lambda \rightarrow \infty$, we have

$$\left\{ \text{Lt} \frac{b_{\lambda}}{b_{\lambda-2}} - 1 \right\} = 0 \quad (48)$$

$$\text{Let} \quad \text{Lt}_{\lambda \rightarrow \infty} \frac{b_{\lambda}}{b_{\lambda-1}} = l \quad (49)$$

then, we have

$$\text{Lt} \frac{b_{\lambda}}{b_{\lambda-2}} = l^2$$

Therefore (48) becomes

$$(l^2 - 1) = 0$$

Hence from (49)

$$\text{Lt} \frac{b_{\lambda}}{b_{\lambda-1}} = \pm 1 \quad (50)$$

In case $\text{Lt} \frac{b_{\lambda}}{b_{\lambda-1}} = -1$, the series (44) is divergent. And when

$\text{Lt} \frac{b_{\lambda}}{b_{\lambda-1}} = 1$, the series solution for (37) has unit radius of convergence. The

series solution (44) is convergent in the neighbourhood of the origin. We proceed to test the convergence at $x = 1$.

Now, let

$$\frac{b_{\lambda}}{b_{\lambda-1}} = 1 - \varepsilon \quad (51)$$

where ε is a function of λ such that

$$\varepsilon = O \left(\frac{1}{\lambda q} \right) \quad (52)$$

q being positive.

Then we have

$$\frac{b_{2q+\lambda+3}}{b_{\lambda-2}} = (1-\varepsilon)^{2q+5} = 1 - (2q+5)\varepsilon \quad (53)$$

$$\frac{b_{2q+\lambda+1}}{b_{\lambda-2}} = (1-\varepsilon)^{2q+3} = 1 - (2q+3)\varepsilon \quad (54)$$

to the first power of ε .

From (53), (54) and (47), we have, keeping terms of the highest order.

$$-\varepsilon\lambda^2 = \lambda \quad (55)$$

Whence we have

$$\varepsilon = -\frac{1}{\lambda} \quad (56)$$

Hence from (51), we have,

$$\frac{b_{\lambda}}{b_{\lambda-1}} = 1 + \frac{1}{\lambda} + O\left(\frac{1}{\lambda^2}\right) \quad (57)$$

if we do not neglect higher powers of ε than the first (57) shows that the series solution (44) is divergent for $x=1$ (Gauss Rule).

Hence, we have, by an extension of Abel's theorem to series divergent on the circle of convergence,

$$\lim_{x \rightarrow 1} \sum_{\lambda=0}^{\infty} b_{\lambda} x^{\lambda} = \sum_{\lambda=0}^{\infty} b_{\lambda} = \infty \quad (58)$$

Thus the amplitude of oscillations increase without limit as we approach the surface of the star.

Now consider the solution of equation (38)

As in the case of equation (37), we can show the series for the complementary function of (38) to be divergent.

For the particular integral of (38) we note that Q is a function of a_1 , and, hence, diverges, as we have proved a_1 to be divergent. Hence the particular integral of (38) is divergent.

Therefore no convergent series solution for (38) can be found.

The series solution for (39) can similarly be shown to be divergent.

Hence all a_1 , a_2 and a_3 in the expression (18) for ξ_1 are infinite.

Also it is impossible for the boundary conditions (33), (34), (35) to be satisfied, as a_1 , a_2 and a_3 do not remain finite at $x=1$.

Hence we see that ξ_1 given by (18) can not remain finite, and the conclusion is that no radial mode of oscillations are possible in this case.

Case II. The density varies as the p^{th} power of the distance from the centre (where p is a positive integer excluding 1 and 3), except in a small, finite core of constant density surrounding the centre.

Let a small core of radius a inside the star of radius R have uniform density, and let the density ρ_0 of the undisturbed state outside the core at a distance ξ_0 from the centre ($a \leq \xi_0 \leq R$) be

$$\rho_0 = k/\xi_0^p \quad (59)$$

Let ρ_a be the undisturbed uniform density of a small core of radius $a = \mu R$ (60) where R is the radius of the star.

And let $\bar{\rho}$ be the mean density in the annulus. We have

$$\rho_a = \frac{k}{a^p} = \frac{k}{R^p \cdot \mu^p} \quad (61)$$

$$\text{and } \frac{4\pi}{3} \bar{\rho} (R^3 - a^3) = \frac{4\pi k}{p-3} \left[\frac{1}{a^{p-3}} - \frac{1}{R^{p-3}} \right], \text{ if } p \neq 3 \quad (62)$$

From (60), (61) and (62), we have

$$k = \{ \bar{\rho} (p-3) \mu^{p-3} (1-\mu^3) R^p \} / 3 (1-\mu^{p-3}) \quad (63)$$

$$\text{and } \bar{\rho} = \{ 3 \rho_a (1-\mu^{p-3}) \mu^3 \} / (p-3) (1-\mu^3) \quad (64)$$

The undisturbed value of gravity, g_0 , at a point ξ_0 is given by

$$g_0 = \left[\frac{4}{3} \pi \rho_a a^3 G + \frac{4\pi k}{p-3} \left\{ \frac{1}{a^{p-3}} - \frac{1}{\xi_0^{p-3}} \right\} G \right] / \xi_0^2 \quad (65)$$

where G is the gravitational constant.

From (61) and (65), we have

$$\begin{aligned} g_0 &= \frac{\pi k G}{3 (p-3)} \cdot \frac{1}{\xi_0^2} \left(\frac{p}{a^{p-3}} - \frac{3}{\xi_0^{p-3}} \right) \\ &= \frac{4\pi k G}{3 (p-3) R^{p-1} \cdot \mu^2} \cdot \left(\frac{p}{a^{p-3}} - \frac{3}{x^{p-3}} \right) \end{aligned} \quad (66)$$

where $\xi_0 = Rx$ ($\mu \leq x \leq 1$)

Integrating the hydrostatic equation of equilibrium in the undisturbed state, viz,

$$\frac{dP_0}{d\xi_0} = -g_0 \rho_0$$

we have, for the pressure P_0 at ξ_0 ,

$$P_0 = \frac{4\pi k^2 G}{3 (p-3) R^{2p-2}} \left\{ \frac{p}{(p+1) \mu^{p-3}} \left(\frac{1}{x^{p+1}} - 1 \right) - \frac{3}{2p-2} \left(\frac{1}{x^{2p-2}} - 1 \right) \right\} \quad (67)$$

assuming that the pressure vanishes on the boundary.

Hence, we have

$$v = \frac{g_0 \rho_0 \xi_0}{P_0} = \frac{(p+1)(2p-2)(px^{p-3} - 3\mu p^{-3})}{p(2p-2)x^{p-3}(1-x^{p+1}) - 3(p+1)\mu p^{-3}(1-x^{2p-2})} \quad (68)$$

$$\text{Also let } m = \frac{\mu(g+2)l^2}{4\pi k R^{2q-p+3}} \quad (69)$$

where μ is permeability and is different from $\mu = \frac{a}{R}$.

Substituting from 66, 67, and 68 in equation (23) we have for the annular region:—

$$\begin{aligned} & [x^{2q-p+5} \{ -3(p+1)\mu p^{-3} \} + x^{2q+2} p(2p-2) - x^{2q+p+3} \\ & \quad \{ 2p(p-1) - 3(p+1)\mu p^{-3} \}] \frac{d^2 a_1}{dx^2} + \\ & [x^{2q-p+4} \cdot 6\mu p^{-3} (p+1)(p-3) - 2x^{2q+1} p(p-1)(p-3) + 4x^{2q+p+2} \\ & \quad \{ 3(p+1)\mu p^{-3} - 2p(p-1) \} + m \{ 2p(p-1)x^{p-2} - x^{2p-1} \\ & \quad \{ 2p(p-1) - 3(p+1)\mu p^{-3} \} - 3(p+1)\mu p^{-3} x \}] \frac{da_1}{dx} + [fx^{2q+3} + \\ & + 6x^{2q-p+3} \alpha \mu p^{-3} (p^2-1) - 2x^{2q} \alpha p(p^2-1) - 2m(q+1) \{ 2p(p-1)x^{p-3} \\ & - x^{2p-2} \{ 2p(p-1) - 3(p+1)\mu p^{-3} \} - 3(p+1)\mu p^{-3} \}] a_1 = 0 \end{aligned} \quad (70)$$

$$\text{Where } f = \frac{6n^2 \cdot (p^2-1)(p-3)R^p \mu p^{-3}}{4\pi k G \gamma}$$

We assume for the solution of (70) the following series

$$a_1 = x^c \sum_{\lambda=0}^{\infty} b_{\lambda} x^{\lambda} \quad (71)$$

As the differential equation (70) has an irregular singularity at the origin the indicial equation gives only one root

$$c = 2(q+1) \quad (72)$$

where b_0 is arbitrarily assumed to be equal to one. (as the differential equation is linear)

Now to find out the recurrence formula equating the coefficient of $x^{2q+\lambda+c-p+3}$, we get a 7-term recurrence formula

$$\begin{aligned}
 & -b_{\lambda} (c+\lambda) (c+\lambda-1) 3(p+1) \mu^{p-3} + 2p(p-1) b_{\lambda-p+3}^{(c+\lambda-p+3)} (\lambda+c-p+2) - \left\{ 2p(p-1) \right. \\
 & \left. - 3(p+1) \mu^{p-3} \right\} b_{\lambda-2p+2} \left\{ (c+\lambda-2p+2) (c+\lambda-2p+1) \right\} + b_{\lambda} (c+\lambda) 6\mu^{p-3} \\
 & (p+1) (p-3) - 2p(p-1) (p-3) b_{\lambda-p+3}^{(c+\lambda-p+3)} + 4 \left\{ 3(p+1) \mu^{p-3} - 2p(p-1) \right\} \\
 & b_{\lambda-2p+2}^{(c+\lambda-2p+2)} + m \left[2p(p-1) b_{2q+\lambda-2p+6}^{(c+\lambda+2q-2p+6)} - \left\{ 2p(p-1) - 3(p+1) \mu^{p-3} \right\} \right. \\
 & \left. b_{2q+\lambda-3p+5}^{(c+2q+\lambda-3p+5)} - 3(p+1) \mu^{p-3} b_{2q+\lambda-p+3}^{(c+\lambda+2q-p+3)} \right] + f b_{\lambda-p} + 6\alpha \mu^{p-3} \\
 & (p^2-1) b_{\lambda} - 2\alpha p(p^2-1) b_{\lambda-p+3} - 2m(q+1) \left[2p(p-1) b_{2q+\lambda-2p+6} - \right. \\
 & \left. \left\{ 2p(p-1) - 3(p+1) \mu^{p-3} \right\} b_{2q+\lambda-3p+5} - 3(p+1) \mu^{p-3} b_{\lambda+2q-p+3} \right] = 0 \quad (73)
 \end{aligned}$$

Arranging in powers of λ and dividing by $b_{\lambda-2p+2}$

$$\begin{aligned}
 & \lambda^2 \left[-3(p+1) \mu^{p-3} \frac{b_{\lambda}}{b_{\lambda-2p+2}} + 2p(p-1) \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} - \left\{ 2p(p-1) - 3(p+1) \right. \right. \\
 & \left. \left. \mu^{p-3} \right\} \right] + \lambda \left[-3(p+1) \mu^{p-3} (4q+3) \frac{b_{\lambda}}{b_{\lambda-2p+2}} + 2p(p-1) (4q-2p+9) \right. \\
 & \left. \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} - \left\{ 2p(p-1) - 3(p+1) \mu^{p-3} \right\} (4q-4p+7) + 6 \mu^{p-3} (p+1) (p-3) \right. \\
 & \left. \frac{b_{\lambda}}{b_{\lambda-2p+2}} - 2p(p-1) (p-3) \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} + 4 \left\{ 3(p+1) \mu^{p-3} - 2p(p-1) \right\} \right. \\
 & \left. + m \left[2p(p-1) \frac{b_{2q+\lambda-2p+6}}{b_{\lambda-2p+2}} - \left\{ 2p(p-1) 3(p+1) \mu^{p-3} \right\} \frac{b_{2q+\lambda-3p+5}}{b_{\lambda-2p+2}} \right. \right. \\
 & \left. \left. - 3(p+1) \mu^{p-3} \frac{b_{2q+\lambda-p+3}}{b_{\lambda-2p+2}} \right] + \left[-6(p+1) (q+1) (2q+1) \frac{b_{\lambda}}{b_{\lambda-2p+2}} \right] \right]
 \end{aligned}$$

$$\begin{aligned}
& + 2p(p-1)(2q-p+5)(2q-p+4) \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} - \left\{ 2p(p-1) - 3(p+1)\mu^{p-3} \right\} (2q-2p+4) \\
& (2q-2p+3) + 12\mu^{p+3} (p+1)(p-3)(q+1) \frac{b_{\lambda}}{b_{\lambda-2p+2}} - 2p(p-1)(p-3) \\
& (2q-p+5) \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} + 4 \left\{ 3(p+1)\mu^{p-3} - 2p(p-1) \right\} (2q-2p+4) \\
& + m \left[2p(p-1)(4q-2p+8) \frac{b_{2q+\lambda-2p+6}}{b_{\lambda-2p+2}} - \left\{ 2p(p-1) - 3(p+1)\mu^{p-3} \right\} \right. \\
& \left. (4q-3p+7) \frac{b_{2q+\lambda-3p+5}}{b_{\lambda-2p+2}} - 3(p+1)\mu^{p-3} (4q-p+5) \frac{b_{2q+\lambda-p+3}}{b_{\lambda-2p+2}} \right] \\
& + f \frac{b_{\lambda-p}}{b_{\lambda-2p+2}} + 6\alpha\mu^{p-3}(p^2-1) \frac{b_{\lambda}}{b_{\lambda-2p+2}} - 2\alpha p(p^2-1) \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} \\
& - 2m(q+1) \left[2p(p-1) \frac{b_{2q+\lambda-2p+6}}{b_{\lambda-2p+2}} + \left\{ 3(p+1)\mu^{p-3} - 2p(p-1) \right\} \right. \\
& \left. \frac{b_{2q+\lambda-3p+5}}{b_{\lambda-2p+2}} - 3(p+1)\mu^{p-3} \frac{b_{2q+\lambda-p+3}}{b_{\lambda-2p+2}} \right] = 0 \quad (74)
\end{aligned}$$

Now we divide by λ^2 and proceeding to the limit as $\lambda \rightarrow \infty$, we have

$$p(2p-2) \left\{ 1 - \text{Lt} \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} \right\} = 3(p+1)\mu^{p-3} \left\{ 1 - \text{Lt} \frac{b_{\lambda}}{b_{\lambda-2p+2}} \right\} \quad (75)$$

$$\text{Let } \text{Lt} \frac{b_{\lambda}}{b_{\lambda-1}} = l \quad (76)$$

Then we have

$$\text{Lt} \frac{b_{\lambda-p+3}}{b_{\lambda-2p+2}} = l^{p+1} \quad \text{and} \quad \text{Lt} \frac{b_{\lambda}}{b_{\lambda-2p+2}} = l^{2p-2} \quad (77)$$

Hence (75) reduces to

$$p(2p-2)(1-l^{p+1}) - 3(p+1)\mu^{p-3}(1-l^{2p-2}) = 0 \quad (78)$$

Therefore from (76), and (78), we get

$$\text{Lt } \frac{b_\lambda}{b_\lambda - 1} = l = 1 \quad (79)$$

Hence, the series solution for (70) has unit radius of convergence.

This is convergent in the neighbourhood of the origin right up to the next singularity ($x=1$).

We proceed to test the convergence of (71) at $x=1$

From (79) we have all the terms ultimately to be of the same sign, and

$$\frac{b_\lambda}{b_\lambda - 1} = 1 - \varepsilon \quad (80)$$

Where ε is a function of λ such that

$$\varepsilon = O\left(\frac{1}{\lambda^p}\right)$$

p being positive.

Then we have

$$\left. \begin{aligned} \frac{b_\lambda}{b_\lambda - 2p + 2} &= (1 - \varepsilon)^{2p-2} = 1 - (2p-2)\varepsilon \\ \frac{b_{\lambda-p+3}}{b_\lambda - 2p + 2} &= (1 - \varepsilon)^{p+1} = 1 - (p+1)\varepsilon \\ \frac{b_{2q+\lambda-2p+6}}{b_\lambda - 2p + 2} &= (1 - \varepsilon)^{2q+4} = (1 - \overline{2q+4}\varepsilon) \\ \frac{b_{2q+\lambda-3p+5}}{b_\lambda - 2p + 2} &= (1 - \varepsilon)^{2q-p+3} = 1 - (2q-p+3)\varepsilon \\ \frac{b_{2q+\lambda-p+3}}{b_\lambda - 2p + 2} &= (1 - \varepsilon)^{2q+p+1} = 1 - (2q+p+1)\varepsilon \end{aligned} \right\} \quad (81)$$

From (74) and (81) we have, keeping terms of the highest order

$$-\varepsilon \lambda^2 \left(p - \mu p - 3 \right) = \lambda \left(p - \mu p - 3 \right) \quad (82)$$

$$\therefore \varepsilon = - \frac{1}{\lambda} \quad (83)$$

Hence, from (80) we have

$$\frac{b_\lambda}{b_\lambda - 1} = 1 + \frac{1}{\lambda} + O\left(\frac{1}{\lambda^2}\right) \quad (84)$$

if we do not neglect higher powers of ϵ than the first.

(84) shows that the series solution (71) is divergent at $x = 1$.

With proper substitution equation (24) reduces to

$$\begin{aligned} & \left[x^{2q-p+5} \left\{ -3(p+1) \mu^{p-3} \right\} + x^{2q+2} p(2p-2) - x^{2q+p+3} \left\{ 2p(p-1) - \right. \right. \\ & \left. \left. 3(p+1) \mu^{p-3} \right\} \right] \frac{d^2 a_2}{dx^2} + \left[x^{2q-p+4} 6\mu^{p-3} (p+1)(p-3) - 2x^{2q+1} p(p-1)(p-3) \right. \\ & \left. + 4x^{2q+p+2} \left\{ 3(p+1) \mu^{p-3} - 2p(p-1) \right\} - m \left\{ 2p(p-1)x^{p-2} - x^{2p-1} \right. \right. \\ & \left. \left. \left\{ 2p(p-1) - 3(p+1) \mu^{p-3} \right\} - 3(p+1) \mu^{p-3} x \right\} \frac{da_2}{dx} + \left[f' x^{2q+3} + 6x^{2q-p+3} \right. \right. \\ & \left. \left. \alpha \mu^{p-3} (p^2-1) - 2x^{2q} \alpha p (p^2-1) + 2m(q+1) \left\{ 2p(p-1)x^{p-3} - x^{2p-2} \right. \right. \right. \\ & \left. \left. \left. \left\{ 2p(p-1) - 3(p+1) \mu^{p-3} \right\} - 3(p+1) \mu^{p-3} \right\} \right] a_2 = Q \end{aligned} \quad (85)$$

$$\text{Where } f' = \frac{6n^2}{\pi K G \gamma} (p^2-1)(p-3) R^p \mu^{p-3}$$

and Q is given by (27)

As in the case of equation (70), we can show the series for the complementary function of (85) to be divergent.

For the particular integral of (85) we see that Q is a function of a_1 and, hence, diverges, as we have proved a_1 to be divergent. Hence the particular integral of (85) is divergent.

Therefore no convergent series solution for (85) can be found.

The equation (25) becomes

$$\begin{aligned} & \left[x^{2q-p+5} \left\{ -3(p+1) \mu^{p-3} \right\} + x^{2q+2} p(2p-2) - x^{2q+p+3} \left\{ 2p(p-1) - \right. \right. \\ & \left. \left. 3(p+1) \mu^{p-3} \right\} \right] \frac{d^2 a_2}{dx^2} + \left[x^{2q-p+4} 6\mu^{p-3} (p+1)(p-3) - 2x^{2q+1} p(p-1)(p-3) \right. \\ & \left. + 4x^{2q+p+2} \left\{ 3(p+1) \mu^{p-3} - 2p(p-1) \right\} - m \left\{ 2p(p-1)x^{p-2} - x^{2p-1} \right. \right. \end{aligned}$$

$$\left\{ 2p(p-1) - 3(p+1)\mu^{p-3} \right\} - 3(p+1)\mu^{p-3} \left[\frac{da_3}{dx} + \left[6x^{2q-p+3} \alpha \mu^{p-3} \right. \right. \\ \left. \left. (p^3 - 1) - 2x^{2q} \alpha p (p^2 - 1) - 2m(q+1) \left\{ 2p(p-1)x^{p-3} - x^{2p-2} \left\{ 2p(p-1) - \right. \right. \right. \right. \right. \\ \left. \left. \left. 3(p+1)\mu^{p-3} \right\} - 3(p+1)\mu^{p-3} \right\} \right] a_3 = Q \quad (86)$$

where Q is given by (27)

The series solution for (86) can similarly be shown to be divergent. Hence none of a_1 , a_2 and a_3 in the expression (18) for ξ_1 is finite.

The boundary conditions (33), (34) and (35) follow from, (23), (24) and (25) when a_1 , a_2 and a_3 are finite.

In this case we obtain the corresponding boundary conditions as follows. Dividing 23, 24 and (25) by v we have

$$\frac{a_1''}{v} + \left[\frac{4-v}{v\xi_0} - \frac{S}{v\xi_0^{2q+4}} \right] a_1' + \left[\frac{n^2\rho_0}{P_0 v \gamma} - \frac{\alpha}{\xi_0^2} - \frac{2(q+1)S}{v\xi_0^{2q+5}} \right] a_1 = 0 \quad (87)$$

$$\frac{a_2''}{v} + \left[\frac{4-v}{v\xi_0} - \frac{S}{v\xi_0^{2q+4}} \right] a_2' + \left[\frac{4n^2\rho_0}{P_0 v \gamma} - \frac{\alpha}{\xi_0^2} + \frac{2(q+1)S}{v\xi_0^{2q+5}} \right] a_2 = Q =$$

$$\left\{ \frac{1}{2} (3\gamma-1) \frac{n^2\rho_0}{P_0 v \gamma} - \frac{3}{4} (\gamma-1) \frac{\alpha}{\xi_0^2} - \frac{S}{\xi_0^{2q+5}} \frac{(q+1)(2q+3)}{2v} \right\} a_1^2 + \xi_0 a_1 a_1'$$

$$\left[\frac{2q+3}{2v} \frac{S}{\xi_0^{2q+5}} + \frac{1}{2} (\gamma+1) \left\{ \frac{n^2\rho_0}{P_0 v \gamma} - \frac{\alpha}{\xi_0^2} \right\} \right] + \left\{ \frac{1}{v} - \frac{1}{4} (\gamma+1) \right\} a_1'^2 \quad (88)$$

and

$$\frac{a_3''}{v} + \left[\frac{4-v}{2\xi_0} - \frac{S}{v\xi_0^{2q+4}} \right] a_3' + \left[-\frac{\alpha}{\xi_0^2} - \frac{2(q+1)}{v\xi_0^{2q+5}} \right] a_3 =$$

$$\left\{ \frac{1}{2} (3\gamma-1) \frac{n^2\rho_0}{P_0 v \gamma} - \frac{3}{4} (\gamma-1) \frac{\alpha}{\xi_0^2} - \frac{S}{\xi_0^{2q+5}} \frac{(q+1)(2q+3)}{2v} \right\} a_1^2 + \xi_0 a_1 a_1'$$

$$\left[\frac{2q+3}{2v} \frac{S}{\xi_0^{2q+5}} + \frac{1}{2} (\gamma+1) \left\{ \frac{n^2\rho_0}{P_0 v \gamma} - \frac{\alpha}{\xi_0^2} \right\} \right] + \left\{ \frac{1}{v} - \frac{1}{4} (\gamma+1) \right\} a_1'^2 \quad (89)$$

Now when $x=1$

$$P_0 = 0$$

$$P_0 v = g_0 \rho_0 \xi_0 = \left[\frac{4\pi K^2 G}{3(p-3) R^{2p-2}} \cdot \frac{\rho x^{p-3} - 3\mu^{p-3}}{x^{2p-1} / v^{p-3}} \right]_{x=1}$$

$$= \frac{4\pi K^2 G (p-3) \mu p^{-3}}{3(p-3) R^{2p-2} \mu p^{-3}} \quad \text{a finite quantity.}$$

and $\nu \rightarrow \infty$, as $P_0 = 0$ and $\xi_0 = R$

$$\text{and } \frac{S}{\nu \xi_0^{2q+5}} = \frac{\mu l^2 (q+2)}{4\pi K R^{2q-p+5, \nu}} \rightarrow 0 \text{ as } \nu \rightarrow \infty$$

similarly

$$\frac{S}{\nu \xi_0^{2q+4}} \rightarrow 0 \text{ as } \nu \rightarrow \infty.$$

Hence, equations (87) and (88) become for finite a_1 and a_2

$$a_1' + \left(\frac{\alpha}{R} - \frac{n^2}{\gamma g_0} \right) a_1 = 0 \quad (90)$$

$$\begin{aligned} \text{and } a_2' + \left(\frac{\alpha}{R} - \frac{4n^2}{\gamma g_0} \right) a_2 + \left\{ \frac{1}{2} (3\gamma - 1) \frac{n^2}{\gamma g_0} - \frac{3}{4} (\gamma - 1) \frac{\alpha}{R} \right\} a_1^2 + \\ \frac{1}{2} (\gamma + 1) \left\{ \frac{n^2}{\gamma g_0} - \frac{\alpha}{R} \right\} R a_1 a_1' - \frac{1}{4} (\gamma + 1) R a_1'^2 = 0 \end{aligned} \quad (91)$$

Now from (90)

$$\frac{n^2}{\gamma g_0} a_1^2 = a_1 a_1' + \frac{\alpha}{R} a_1^2$$

Hence, we have

$$\begin{aligned} \frac{1}{2} (3\gamma - 1) \frac{n^2}{\gamma g_0} a_1^2 - \frac{3}{4} (\gamma - 1) \frac{\alpha}{R} a_1^2 &= \left\{ \frac{1}{2} (3\gamma - 1) - \frac{3}{4} (\gamma - 1) \right\} \\ &\quad \frac{\alpha}{R} a_1^2 + \frac{1}{2} (3\gamma - 1) a_1 a_1' \\ &= \frac{1}{4} \frac{\alpha(3\gamma + 1)}{R} a_1^2 + \frac{1}{2} (3\gamma - 1) a_1 a_1' \end{aligned}$$

Also we have from (90)

$$a_1'^2 = \left(\frac{n^2}{\gamma g_0} - \frac{\alpha}{R} \right) a_1 a_1'$$

Hence, we get

$$\begin{aligned} \frac{1}{2} (\gamma + 1) \left\{ \frac{n^2}{\gamma g_0} - \frac{\alpha}{R} \right\} R a_1 a_1' - \frac{1}{4} (\gamma + 1) R a_1'^2 &= \frac{1}{2} (\gamma + 1) R a_1'^2 \\ &\quad - \frac{1}{4} (\gamma + 1) R a_1'^2 \\ &= \frac{1}{4} (\gamma + 1) R a_1'^2 \end{aligned}$$

Therefore equation (91) becomes

$$a_2' + \left(\frac{\alpha}{R} - \frac{4n^2}{\gamma g_0} \right) a_2 + \frac{1}{4} \frac{\alpha(3\gamma+1)}{R} a_1^2 + \frac{1}{2} (3\gamma-1) a_1 a_1' + \frac{1}{4} (\gamma+1) R a_1'^2 = 0 \quad (92)$$

Similarly, we have, when a_3 is finite,

$$a_3' + \frac{\alpha}{R} a_3 + \frac{1}{4} \frac{\alpha(3\gamma+1)}{R} a_1^2 + \frac{1}{2} (3\gamma-1) a_1 a_1' + \frac{1}{4} (\gamma+1) R a_1'^2 = 0 \quad (93)$$

Equations (90), (92) and (93) are the boundary conditions which are the same as the conditions for the case when there is no magnetic field.

It is impossible for the boundary conditions to be satisfied, as a_1 , a_2 and a_3 do not remain finite at $x=1$

As a_1 is the predominating first order term in the expression for ξ_1 in (18), ξ_1 becomes infinitely great when $x=1$.

The conclusion, therefore, is that no mode of radial oscillation is possible in this case too.

¹⁰In the opinion of Kopal (1938) δ cephei-F₅ stars seem to approach the limit of homogeneity, Chandrasekhar stated in 1938 that the giants should be more homogeneous than the main series stars.

The Cepheids and Cluster-type variables which occur in the "super-giant" regions of Hertzsprung-Russell diagram must be much less concentrated towards the centre than the typical main series stars. Eddington has also emphasised that the Cepheids should necessarily be more homogeneous than ordinary stars.

Hence a passing star will bring about some sort of resonance phenomenon by increasing the amplitude of pulsation through tidal influence and making the system unstable, so that matter rejected to suitable distances to be formed into planets.

If I_1 is the kinetic energy of revolution of the planets including the asteroids and the satellites round the sun, it could be shown that $I_1 = \frac{2\pi^2 \gamma_E^2}{T_E^2} \sum \frac{M}{\gamma}$

Where M mass of a planet and r semi-axis major of its orbit

M_E = mass of the earth and γ_E semi major-axis of earth's orbit

T_E = sidereal period of the earth's revolutions round the sun

It can be seen that $I_1 < 3 \times 10^{42}$ ergs. If I_2 is the kinetic energy of the planets including satellites and asteroids then $I_2 = \frac{4\pi^2}{5} \sum \frac{Mk^2}{t^2}$ where t is the

period for the axial rotation of a planet. It can be seen that $I_2 < 10^{42}$ ergs. The gravitational energy of the planet and satellites is $W = \frac{1}{2} \sum MV$ where V is the gravitational potential at the planet of mass M due to the sun's attraction.

Hence $W = \frac{v}{2} \odot \approx \frac{M}{\gamma}$ where \odot is the sun's mass and v is the constant of gravitation.

We found that $W \sim 2 \times 10^{42}$ ergs

Hence the total energy of the planetary system $I_1 + I_2 + W < 6 \times 10$ ergs.⁴²

According to Eddington the total store of available heat energy and radiant energy of the sun consists of 2.97×10^{48} ergs in the form of material kinetic energy, radiant energy and an unknown amount of energy of ionisation and excitation which is somewhat less than 2.7×10^{48} ergs. It will not be unreasonable to take the total available energy at least to be 3×10^{48} ergs. The total mass of the planets would lie between $\odot/500$ and $\odot/1000$. Hence the total energy stored up in them when they were not separated from the sun would be at least 3×10^{48} . This is at least 5000 times the present energy of the planets.

Let us take the mass of the parent Cepheid to be that of the representative Cepheid, Cepheid which is nine times the sun's mass. Taking Eddington's figure for the radius R of the star $= 2.32 \times 10^{32}$ c.m. the negative gravitational potential energy in contracting from infinite diffusion to present radius $R =$

$$\frac{3}{2} \frac{v (9\odot)^2}{R} \sim 1.4 \times 10^{49} \text{ ergs from which we get material kinetic energy, radiant}$$

energy and the energy of ionisation and excitation. Now on account of dynamical instability caused by near-by passage of a star of mass of the same order as δ cepheid, material will be ejected from the parent Cepheid. The energy required in ejecting material of mass more or less equal to that of the sun to a sufficient distance was calculated so that both the sun and a part of the planetary ribbon that is formed may escape recapture by the parent star.

The average differential velocity between two star is about 20km/per sec. As the ejected material had originally been a part of the parent star, the differential velocity between the parent star and the ejected material due to near-by passage of a star can hardly exceed 10Km/sec.

If we take the differential velocity to be 8 Km/per sec for the ejected material with a part of the planetary ribbon, then in order to escape capture by the parent

Cepheid it must be ejected to a distance greater than d given by $v^2 = 2 \frac{v(8\odot + \odot)}{d}$

where $v = 8$ Km/sec. whence we have $d = \frac{18v\odot}{v^2} \sim 3.6 \times 10^{15}$ cms.

The radius of the parent Cepheid being 2.32×10^{12} cm., the material equal to the Sun's mass will have to be ejected to a distance at least 1600 times the radius of the parent star in order to avoid recapture by it.

The hypothesis is that this ejected material with part of the ribbon ultimately

condensed into our sun and the planets, the passing star as well as the parent Cepheid being responsible for giving orbital motion of the planets round the sun.

Now Pluto is at a distance of 6×10^{14} cms from the sun. If at any instance it comes between the parent Cepheid and the sun, its distance from the parent Cepheid would be at least of the order 3×10^{15} cms.

As $\frac{8\odot}{(3 \times 10^{15})^2} < \frac{\odot}{(6 \times 10^{14})^2}$ there was no chance of Pluto being re-

captured by the parent Cepheid.

There is also no difficulty about angular momentum. The distance of ejection d to avoid recapture by the parent Cepheid should be at least of the order 3.6×10^{15} cms. or greater than 200 Astronomical units. Now taking the angular momentum per unit mass of the earth to be unity; and using the formula $l(1+x)$ for angular momentum per unit mass of the parent Cepheid where l semi-latus rectum 400 astronomical units, and x is the ratio of the mass of the parent cepheid to that of the sun $= 8$, we get the angular momentum per unit mass of the parent cepheid to be $\sqrt{3600}$ units or 60 units. This is more than sufficient to give the necessary angular momentum to the planets to revolve round the sun as the average angular momentum per unit mass for the planetary system is 2.63 units.

According to the present theory, the parent Cepheid would also have a planetary system round it.

The energy required by the sun to be ejected to a distance of escape and to have a velocity of 8 Km/sec is given by

$$W = \frac{1}{2} \odot v^2 + \frac{2}{5} \odot a^2 \omega^2 + \frac{3}{2} v \frac{(\odot)^2}{a} + \frac{1}{2} v \frac{8 \odot^2}{a}$$

where a is the radius of the sun $= 6.95 \times 10^8$ cms, $v = 8$ Km/sec and $\omega =$ angular velocity.

$= \frac{2}{28 \times 24 \times 60^2}$ C. G. S. units as period of the sun's axial rotation is about 28 days.

Substituting these values we get $W < 6 \times 10^{48}$ ergs

The magnetic energy may be taken to be $\frac{\mu H^2}{8\pi}$ per unit volume. The volume

of the parent Cepheid may be taken to be 8 times that of the sun. We can not say what H is for the parent Cepheid or the sun. But it is not unreasonable to suppose that sun with its planetary system has taken away part of the magnetic energy of the parent cepheid.

The sun has therefore taken about 2/5th of the energy of the parent Cepheid. As the passage of a star close to the representative Cepheid need not be grazing or even very near and as only two bodies are involved, our theory makes a less

number of assumptions than any other catastrophic or any fission theory, and is definitely more probable. One conclusion seems irresistible:—If the theory be correct in its essentials, there may be more planetary systems than at present supposed, and if life on earth be the result of an orderly natural process some of the other planets in other systems may be inhabited by beings like us.

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